

DEVELOPMENTS IN THE SYNTHESIS OF
ZWITTERIONIC OLEFIN POLYMERIZATION CATALYSTS

By

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DEVELOPMENTS IN THE SYNTHESIS OF ZWITTERIONIC
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Chairmen: David Richardson/James Boncella
Major Department: Chemistry

Potential methods for the synthesis of zwitterionic, single-site polymerization catalysts were examined, and a number of complexes were prepared. The prepared complexes are early transition metal metallocenes, which are not zwitterionic species, and *ansa*-silyl-bridged cyclopentadienyl-amido (Cp-amido) complexes, some of which are zwitterionic species. In the process of preparing these complexes, model ruthenocene complexes were prepared employing the same ligands, and their reactivity was also examined.

A series of metallocene complexes were prepared by using Cp ligands derived from 6,6-dimethylfulvene. The addition of lithium diisopropylamide (LDA) to 6,6-dimethylfulvene leads to deprotonation of the β -exo carbon and the synthesis of the anionic methylvinyl-Cp, CpC_3H_5 , ligand. This ligand was used to prepare a series of metallocenes, and the

reactivity of these complexes toward hydroboration with $\text{Ph}_2\text{BH}\cdot\text{Py}$ was examined. The ruthenocene reacted with the borane yielding reduction of the double bond. However, with zirconocenes, reactivity was observed between the borane and the metal center. With the dimethyl zirconocene, this led to a new complex whose structure is proposed based on spectroscopic data.

A new Cp ligand, also based on 6,6-dimethylfulvene, was prepared by the addition of (*p*-bromo- or (*p*-iodophenyl)lithium to 6,6-dimethylfulvene. This yielded the anionic Cp ligand $\text{CpC}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{X}$ ($\text{X}=\text{Br}, \text{I}$) from which was prepared a number of metallocenes. When an 18 electron ruthenocene complex was prepared with the ligand, halo-lithium exchange occurred at the ligand, and trapping the resulting lithiate with boranes yielded a borate-containing ruthenocene, and a borane-containing ruthenocene. Similar chemistry was attempted with 16 electron zirconium complexes, however reactivity occurred at the metal center.

Since it was not possible to prepare borate-containing metal complexes after the ligand was coordinated to early transition metals, methods for preparing the borate-containing ligand prior to coordination were examined. Preliminary studies using tin-coupling methods appear promising for the synthesis of borate-containing metallocenes, and more work is required to fully understand these systems. The use of silyl-bridged cyclopentadienyl-amido ligands has proven to be a very successful method for the synthesis of borate-containing ligands, and metal complexes containing these ligands have been prepared. In the process, a series of borate-containing aniline derivatives have been prepared, which appear to have a great deal of potential as ligands in transition metal chemistry.

CHAPTER 1 INTRODUCTION

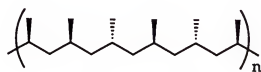
History of Heterogeneous Systems.

While studying the formation of long-chain trialkylaluminum compounds *via* the insertion of ethylene into Al-C bonds, Karl Ziegler and coworkers made a serendipitous discovery. When trace amounts of a nickel compound were left from a previous hydrogenation reaction in the autoclave, the only product observed was 1-butene. This became known as the "nickel effect," and led Ziegler to examine the effect of other heavy metals on the insertion reaction. Then, in late 1953, Ziegler and coworkers¹ found that the presence of zirconium acetylacetonate during the reaction led exclusively to high molecular weight polyethylene (HMWPE) at ambient temperatures and pressures. This discovery was astonishing considering polyethylene (PE) was previously only prepared by a radical mechanism under extremely harsh conditions of high temperature and pressure.

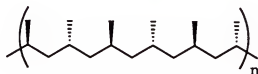
Ziegler and coworkers² soon established that the best catalyst systems for the polymerization of ethylene to high density polyethylene (HDPE) consisted of a group 4 metal chloride (Zr(III), Zr(IV), Ti(III), or Ti(IV)) and a trialkyl aluminum cocatalyst, with the best catalyst system being a combination of TiCl_4 and triethylaluminum. However, at this time, the active site had not yet been determined, and arguments were presented about

whether the aluminum species or the transition metal species served as the active site.

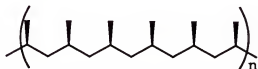
The first major contributor to this new chemistry was Natta and coworkers³, who discovered that by using Ziegler's catalyst system, higher α -olefins (namely propylene) could be polymerized with high stereospecificity. Although there is some speculation about how Natta learned of the Mülheim process (as this low temperature and pressure polymerization reaction was called by Ziegler), there is little doubt about the immense contribution to this chemistry by Natta's group. They quickly and efficiently devised methods for determining the structure of stereoregular polymers which are still used today.



atactic polypropylene



syndiotactic polypropylene

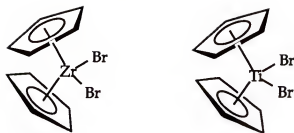


isotactic polypropylene

Figure 1-1. The stereospecific structure of the three main types of polypropylene

Higher α -olefins, such as propylene, can be polymerized to give polymers with different stereoregular structures, and there are three major types produced (Figure 1-1). For simplicity, we will use polypropylene as an example. Atactic polypropylene has a random orientation of methyl groups along the polymer backbone and lacks any crystallinity. This material is usually a waxy or oily material and has limited commercial uses. Syndiotactic polypropylene has methyl groups with alternating configurations along the polymer backbone, and due to this regular pattern, is a much more crystalline polymer. However, there has been no real commercial use found for syndiotactic propylene as of yet. Homogeneous catalysts that give high selectivity for syndiotactic polypropylene have only been developed within the last 10 years. Therefore, more uses for this material may still arise. Isotactic polypropylene is the most widely used polypropylene, and has methyl groups with identical configurations along the polymer backbone. This polymer, which is predominantly prepared by heterogeneous catalysts, is highly crystalline and has many commercial uses, especially in packaging and containers.⁴

It is interesting to note that while Ziegler and Natta were quickly expanding the frontiers of polymer science, Wilkinson and coworkers were developing new transition metal complexes that would eventually replace the systems designed by Ziegler. In early 1953, Wilkinson and coworkers⁵ first reported the synthesis of new bis-cyclopentadienyl (Cp) derivatives of some transition elements, including Cp_2TiBr_2 and Cp_2ZrBr_2 . These complexes



were prepared during Wilkinson's ongoing examination of new metallocene complexes following his elucidation of the correct structure of ferrocene in 1952. Similarly, in 1954, Wilkinson and Birmingham⁶ reported the synthesis of a series of group 4 metallocene halides, along with other transition metal metallocenes. This work became most important when, in 1959, Breslow and Newburg⁷ reported the polymerization of ethylene with a homogeneous catalyst system composed of Cp_2TiCl_2 and various dialkyl- and trialkylaluminum compounds. This landmark study spawned one of the largest and fastest technological races that has ever occurred, and some estimate that over \$3 billion⁸ has been used to further the understanding of this chemistry.

History of Homogeneous Systems.

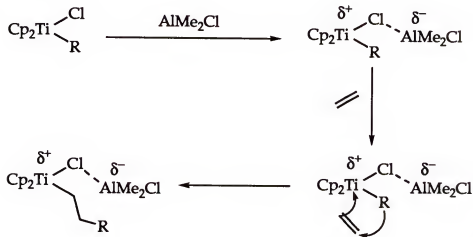
Studies on homogeneous systems were initiated in 1959 by Breslow and Newburg⁷ in order to determine the active site of polymerization, determine the mechanism of polymerization, increase the "surface area" of the catalyst, aid in removal of the catalyst system from the polymer product, and produce a more uniform polymer. The authors found that the addition of dialkylaluminum chlorides or aluminum trialkyls to titanocene dichloride, in toluene or hydrocarbon solvents, led to ethylene

polymerization catalysts with similar or better activity, compared to the heterogeneous systems based on titanium tetrachloride. This study helped dispel the belief of some researchers that the high activity of the Ziegler-catalysts stemmed from their heterogeneity.

The authors observed that the rate of polymerization and the molecular weight of the polymers are independent of the ratio of diethylaluminum chloride to titanocene dichloride. Also, the activity is independent of the aluminum alkyl used, and both diethylaluminum chloride and ethylaluminum dichloride give similar results. Triethylaluminum was the only exception, and the activity observed when it is used as a cocatalyst was much lower than the other aluminum alkyls. However, most intriguing to the authors was the presence of Ti(III) species in the catalyst mixtures, which were observed by the green and blue colors of the catalytic solutions, magnetic susceptibility measurements, analysis of isolated crystalline solids, and titration of hydrolyzed samples with ferric ions. These observations, along with the observation that small amounts of O₂ increased the catalytic activity allowed the authors to propose a mechanism for the polymerization(Scheme 1-1).

The authors concluded that the active catalytic species was a Ti(IV) species, and that O₂ was beneficial because it oxidized any Ti(III) species in solution to Ti(IV). Also, since triethylaluminum reacts much more readily with O₂ than the other chloride containing aluminum alkyls, the observation that triethylaluminum was the worst co-catalyst made sense. The co-catalyst, in the triethylaluminum case, actually inhibited the oxidation of Ti(III) species, thus reducing the amount of active catalyst in the catalytic mixture. The proposed mechanism included the initial complexation of the aluminum species with the titanocene dichloride, leading to a reduced Ti(III)

species. The Ti(III) species can then be re-oxidized to Ti(IV) by O_2 , and alkyl transfer from the aluminum to the Ti leads to a chloride-bridged Ti-Al



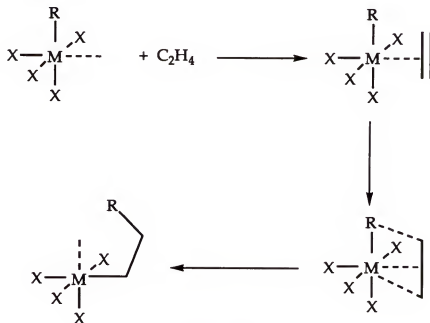
Scheme 1-1

complex. This "active catalyst" could then insert an olefin into the Ti-alkyl bond leading to a propagating polymer chain(Scheme 1-1).

Although many aspects of this mechanism have since been refuted, two important conclusions were made; that the active species is an Ti(IV) species, and that the Ti houses the active site. These conclusions were very instrumental in gaining an understanding about the true catalyst system.

In 1964, Cossee and Arlmann⁹ published back to back articles on the mechanism and structure of Ziegler-Natta catalysts. Although these theoretical studies were on heterogeneous Ziegler-type catalyst systems, the mechanism proposed for olefin polymerization is generally accepted as the correct mechanism for both heterogeneous and homogeneous systems.

Cossee's approach^{9a} to the elucidation of the mechanism involved molecular orbital and ligand field theory, and studied the rearrangement of molecular orbitals upon binding of an olefin to the electron-deficient metal center. The results of this study indicated two main features of the polymerization reaction; that the metal center is in an essentially octahedral environment, and that the polymer chain moves back and forth between two sites on the same metal center. There is no exchange between metal centers in the propagating polymer reaction. Therefore, the following mechanism was proposed (Scheme 1-2).



Scheme 1-2

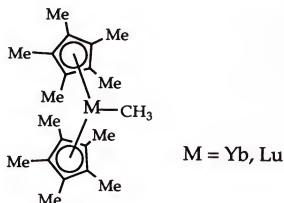
This mechanism successfully explained the driving force of the polymerization reaction in such a way that was consistent with the known kinetic studies by Natta¹⁰ and others. Natta found that the rate of polymerization of propylene with an α - $TiCl_3$ / $AlEt_3$ system was dependent

upon the amount of TiCl_3 and the pressure of the propylene. However, the rate was independent of the Al alkyl concentration. To explain these observations, Cossee proposed two explanations; the binding of the olefin to the metal center is the rate-determining-step, or the olefin insertion into the metal alkyl bond is the rate-determining step. In the second case, a number of olefins bind and then are released before one finally inserts into the metal alkyl bond. Since his calculations showed that there was little change in the molecular orbital energies for the unbound versus the bound olefin, it seemed unlikely that the activation barrier for olefin binding was enough to make that step rate-determining. Therefore, alkyl rearrangement was concluded to be the rate-determining-step, although the experimental activation barrier observed for this rearrangement is relatively low (10 kcal/mol).

With the mechanism of polymerization becoming more understood, researchers could begin to examine effects on polymerization by altering different aspects of the catalyst systems. These methods took three general forms; altering the metal center, altering the ligand environment, and altering the counter-ion/co-catalyst.

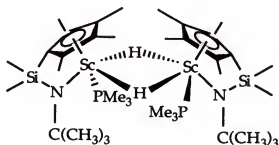
Although a mechanism had now been proposed that was consistent with experimental results, the structure of the active catalyst was still elusive. However, one method that some researchers used to study the mechanism was to change the active metal center from the more common group 4 species, to a more stable, and therefore less reactive group 3 species. Since an active group 3 alkyl species would be a neutral species, it was proposed that intermediates in the polymerization pathway might be observed. The three research groups of Bercaw,¹¹ Marks,¹² and Parshall¹³ examined the effects of organolanthanide complexes for olefin polymerization.

Parshall and Watson¹³ developed the chemistry of the very bulky bis-pentamethylcyclopentadienyl- ytterbium and lutetium alkyls, which were



found to be active catalysts for the polymerization of ethylene. Reported rates of polymerization of at least $115 \text{ g/mmole Lu (min)}^{-1} (\text{kg cm}^2 \text{ of C}_2\text{H}_4)^{-1}$ at $50 - 80^\circ\text{C}$ in cyclohexane are surprisingly fast for such a bulky system. With this system, Parshall's group was able to successfully study many chain transfer and chain termination mechanisms, which are difficult to study with the group 4 systems due to interaction with the counter-ion. However, the system was not able to polymerize or oligomerize higher α -olefins.

Bercaw's group^{11a, 11b} developed the less bulky scandium hydride dimer based on a chelating, silyl-bridged Cp-amido ligand and found the reactivity of this new system to be significantly different than the system of



Parshall. This was not surprising, since the bridged amido ligand should make the metal center much more electrophilic, and thus enhance olefin binding. This ligand was found to oligomerize higher α -olefins such as 1-butene and 1-pentene, although slowly. This new catalyst system showed increased rates over the permethylated systems studied by Parshall, but they still allowed for some ability to follow the polymerization reaction. More importantly, this study developed a new ligand system that would inevitably propel homogeneous group 4 systems into industrial applications. More about the group 4 systems with this ligand will be discussed later.

Marks and coworkers¹² developed a new series of decamethyl-lanthanacenes based on the bulky bis-trimethylsilylmethyl alkyl group. These catalysts are also highly active olefin polymerization and oligomerization catalysts, and the results of the study were compared to the study by Parshall.

These group 3 systems were successfully utilized for the study of some aspects of the polymerization reaction of Ziegler-Natta catalysts. However, their activities remain significantly less than in the group 4 systems and they only, at best, oligomerize higher α -olefins. Therefore, comparisons of the two types of systems require cautious consideration.

As observed with the group 3 systems, altering the ligand environment can have a significant effect on the activity of the catalyst and the properties of the polymer that is formed. With group 4 catalyst systems, these effects have been studied using hundreds of different ligand systems.¹⁴ The effects of changing the ligand environment are observed in two ways; changed activity of the catalyst, or different stereocontrol imparted on the polymer product. Initial studies by Ewen¹⁵ showed that by simply changing the ligand system from zirconocene dichloride to 1,1'-dimethylzirconocene dichloride, the

activity of the resulting catalyst, when activated with methylaluminoxane (MAO), was increased by a factor of 3. The ability to change the ligand environment to control the polymer produced has been one of the most exciting and studied aspects¹⁶ of homogeneous catalysts, and a great deal of fine-tuning has been accomplished with these catalysts in order to selectively prepare any number of polymers with selected properties.

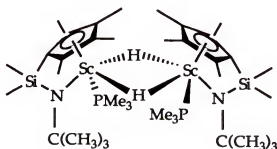
Once the understanding that MAO allowed metallocene catalysts to polymerize propylene, many research groups became interested in the possibility of planned stereocontrol on the polymer by specific metallocene catalysts. This quickly became realized, as the development of chiral metallocenes was already being accomplished.¹⁷ Soon after, the series of ethylene-bridged metallocenes prepared by Brintzinger and co-workers¹⁸ was shown to polymerize propylene to highly isotactic polypropylene. Related work by Ewen¹⁹ on the (en)(thind)₂TiCl₂ / MAO system, and Kaminsky and coworkers²⁰ on the *rac*-(en)(thind)₂ZrCl₂ / MAO also provided similar results. These studies set forth a flood of papers related to stereospecific polymer formation by chiral catalysts.¹⁴

There has been too much work accomplished to fully review these catalyst systems, and since the goal of this dissertation is not related to stereocontrol of polymers, I will not give a detailed description of many of the catalysts. A number of excellent reviews¹⁴ are available to the reader if they desire to learn more about stereospecific polymerization. However, two ligand systems that have been developed in the last 5 years are pertinent to this study, and will be discussed below.

Although the chemical industry has developed homogeneous, single-site catalysts for over 20 years (and supported development in academic laboratories), it was not until a few years ago that single-site catalysts have

become industrially important.⁸ This lack of interest may stem from the relatively high cost of single-site catalysts compared to heterogeneous catalysts, the cost of designing and building new polymerization reactors, or the loss of profit that would occur if one of the current reactors was shut down for conversion to a homogeneous system. However, over time, it became clear that homogeneous catalysts could produce different, and in many cases better polymers than heterogeneous systems. The development of a new class of homogeneous catalysts in the early 90's pushed homogeneous catalysts over the edge from an academic novelty to an industrial tool.

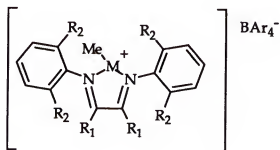
The development of "constrained geometry" or "CpSiNR" scandium complexes by Shapiro, Bercaw and coworkers¹¹ in 1990, was quickly followed by the use of these ligands with group 4 metals.²¹ These ligands (already mentioned) include a bidentate, Cp-amido ligand that can be bridged by either a hydrocarbon chain or silyl group. The most important class of Cp-amido



complexes involves the silyl bridge, which ties back the Cp(centroid)-M-N bite angle significantly (25 - 30 ° smaller), compared to the typical Cp(centroid)-M-Cp(centroid) of metallocenes.²² This, along with the much smaller size of the amido ligand compared to a Cp ligand, increases the size of the active site, and

allows for the copolymerization of larger α -olefins with ethylene. The synthesis of ethylene co-polymerization products is becoming more important as new applications of plastics are being required. Also, the reduced π -donating character of the amido ligand, as well as the reduced electron count of these systems ($12 e^-$), compared to metallocenes ($16 e^-$) leads to a much more Lewis acidic metal center. The result of this enhanced Lewis acidity is observed in the formation of high-molecular-weight polyethylene with reduced branching, presumably due to the ability of the active catalyst to promote facile olefin migratory insertion and reduce typical chain transfer mechanisms. Thus, these catalysts are highly active catalysts when activated with MAO or when used with weakly coordinating anions (WCA), and their industrial importance is reflected in the heated patent rights case between Dow Chemical and Exxon,²¹ two giant polyolefin producers.

Recently, another important class of single-site catalysts have been developed that has again increased the potential of homogeneous catalysts even further beyond traditional heterogeneous catalysts. The report in 1995 by Brookhart and coworkers,²³ that late transition metal diimine catalysts can polymerize ethylene to high-molecular-weight polyethylene, promoted a



great deal of interest in the chemical community. These systems, which traditionally dimerize or oligomerize ethylene, or polymerize ethylene to useless, non-branched polyethylene, can be used to prepare high-molecular-weight polyethylene with various degrees of branching, by using sterically bulky diimine ligands. The purpose of the bulky groups on the diimine ligand is to reduce the propensity of the growing polymer chain to β -hydride eliminate, which is typically a facile chain transfer step in late transition metal catalysts.

Although it is generally accepted²⁴ that the mechanism of polymerization in these Pd(II)- and Ni(II)-diimine catalysts is the same as in the early transition metal systems, the reduced electrophilicity and oxophilicity of the late transition metal systems leads to polymers with different properties. Since the bulky groups on the diimine ligands prevent facile associative displacement of any olefin-terminated bound polymer, the resting state of the active catalyst retains the polymer group and an active site. This allows for practically living polymerization to occur, leading to block copolymers. These copolymers tend to be elastomeric, and there are many potential applications for polymers produced from these catalysts.

Some examples of the control on polymerization reactions imparted by changing the metal center as well as changing the ligand environment has been discussed. However, the third method for controlling the reactivity of polymerization catalysts is perhaps the most interesting, and definitely the method most related to his work. This involves different methods for activating the catalysts, whether *in situ*, or prior to polymerizations by preparing zwitterionic catalyst species.

For more than ten years after Cossee's proposed mechanism, very little progress was accomplished on homogeneous catalysts. This was because the

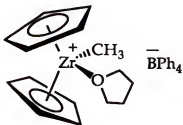
results using homogeneous catalysts activated with alkyl aluminum compounds were often irreproducible. It was not until the late 1970s, when Kaminsky, Sinn, and co-workers²⁵ reported that the addition of small amounts of water to catalyst mixtures of metallocenes activated with aluminum alkyls could lead to significantly increased catalytic activity, that a better understanding of the chemistry could be attained. This was a major discovery, and brought understanding to over ten years of results that had frustrated those trying to understand them. Kaminsky, Sinn, and coworkers found that water reacts with trialkylaluminum complexes to form oligomeric aluminoxanes, which have a general formula $[RAlO]_n$. The most common aluminoxane, methylaluminoxane (MAO), is the hydrolysis product of trimethyl-aluminum. This complex system of cross-linked cyclic and linear species¹ is an excellent initiator for group 4 metallocenes, and it is now generally understood that the MAO can abstract chlorides or alkyl groups from the group 4 metallocene to form the cationic metal-alkyl species. The high activity observed with the MAO systems is most likely due to the weak interaction of the bulky, charge-delocalized MAO anion with the cationic metal center, allowing for easy coordination of the incoming olefin. The major disadvantage to the MAO initiated system is that there is an equilibrium that exists¹ between the inactive catalyst precursor and the active



catalyst system (equation 1-1), and the equilibrium lies far toward the left, or catalyst precursor. In order to initiate a large percentage of the catalyst precursor, a huge excess of the MAO is added, usually on the order of 10^3 mol

MAO / mol Zr. This results in relatively high cost of the active catalyst,⁸ mostly due to that of MAO, as well as a significant amount of aluminum residue left in the polymer product, which must be ultimately removed. In order to avoid this problem, some investigators began to look to other weakly coordinating counter-ions that could stabilize the active catalyst and not interfere with olefin binding.

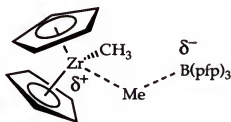
The high electrophilicity of the active metallocenium catalyst requires the use of a very stable, large anion that will not decompose by interaction with the cation. Initial studies²⁶ on typical anions such as PF_6^- and BF_4^- proved this, and salts of with these anions decomposed rapidly with fluoride abstraction by the metal center. Thus other, less reactive anions were examined. Two reports of isolated metallocenium ions were reported in 1986, by Bochmann's group and Jordan's group. Bochmann's group²⁷ prepared and isolated the first cationic titanocene methyl complex $[\text{TiCp}_2\text{Me}(\text{L})]^+\text{X}^-$ where L is various amines, and X^- is PF_6^- or BPh_4^- . Although these complexes are not active polymerization catalysts, they do undergo insertion reactions with nitriles. The lack of reactivity with olefins is clearly due to the strongly Lewis basic amine ligands, which cannot be displaced by the incoming olefin. A more significant report was presented by Jordan and co-workers,²⁸ who reported the crystal structure of the zirconocenium cation with a tetraphenylborate anion. The cationic metal center was isolated as a



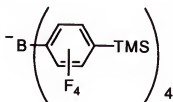
THF adduct, however the THF was labile enough in methylene chloride to allow for the slow polymerization of ethylene. This was the first example of an isolated active catalyst, and showed that MAO was not necessary for polymerization to occur. Of course, the low activity caused by the coordinated THF, along with the slow decomposition of the borate anion made this system less than perfect, but this paved the way for a great deal of research on new, weakly coordinating anions (WCA), which have revolutionized metallocene catalysts.

In 1989, Turner and coworkers²⁹ reported the use of the bulky anionic *nido*-carborane $C_2B_9H_{13}$ as a WCA, and isolated the decamethyl-zirconocenium complex with this anion containing a hydride bridge. This catalyst rapidly polymerized ethylene, and showed the possibility of other types of counterions other than traditional borates. However, most work has focused on the use of more traditional borates.

Many new WCA based upon perfluorinated phenylboranes³⁰ and borates have been developed. Tris-perfluorophenylborane,³¹ first used by Marks and coworkers, is a very strong Lewis acid which is capable of abstracting a methyl group from dimethyl metallocenes. The abstracted methyl group bridges the two highly electrophilic centers, and this allows the vacant coordination site on the metal to be easily accessible by incoming olefins. The result is a highly active polymerization catalyst which has even

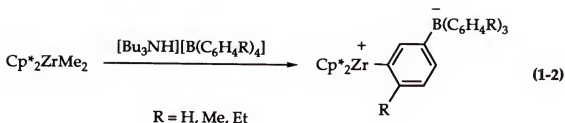


better activities than the catalysts initiated with MAO. Other work has focused on the synthesis of even more strically hindered borates, and Marks and coworkers³² have developed the *para*-TMS derivative of the perfluorinated tetraphenylborate, which also is useful in the preparation of highly active catalysts.

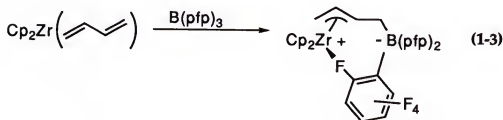


A great deal of interest has been devoted to the development of zwitterionic metallocenium catalysts. Ion pairing between the active metal center and the associated counter-ion plays a large role in the activity and rate of the catalyst system. Also, increased ion separation during the polymerization reaction often leads to catalyst deactivation. One potential method to solve this problem is the synthesis of zwitterionic catalysts. With these zwitterionic species, the ion-pairing, lifetime, and solubility of the active catalyst might be effected. Another more obvious benefit is the ability to use the catalyst straight out of a bottle, without any co-catalyst necessary for activation.

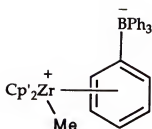
There are many methods for the preparation of zwitterionic catalyst species, however only little success has been accomplished in this area. In 1989, Turner and co-workers²⁹ reported the preparation of a zwitterionic, base-free catalyst system from the addition of $[\text{Bu}_3\text{NH}][\text{B}(\text{C}_6\text{H}_4\text{R})_4]$ to dimethyl decamethylzirconocene (Equation 1-2). This zwitterionic system



rapidly polymerized ethylene; however, the zwitterionic character of the complex is relatively brief, and any chain transfer or chain termination step would lead to a non-zwitterionic salt. Recently, Erker and coworkers³³ have developed a new zwitterionic metallocenium alkyl (Equation 1-3) based on the interaction of $\text{B}(\text{pfp})_3$ with zirconocene butadiene complexes. These are active catalysts for ethylene and propylene, and like the systems by Turner and coworkers, the anion is bound to the growing polymer.

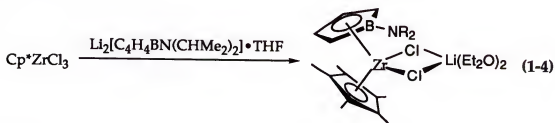


Other temporary zwitterionic systems were developed by Pellechia and co-workers,³⁴ Bochmann and coworkers,³⁵ and Horton and Frijns.³⁶ The systems studied by these groups utilize the η^6 -binding mode of one of the phenyl groups of a tetraphenyl borate. Again, these zwitterionic complexes



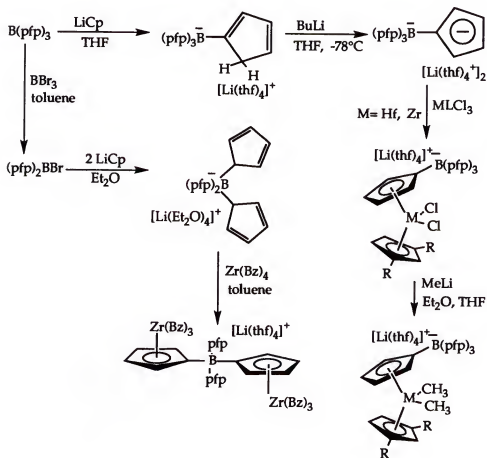
are not active as zwitterionic species, and displacement of the phenyl ligand by an incoming olefin must preclude olefin coordination. Although these complexes are not true zwitterionic polymerization catalysts, they are, once activated, very efficient polymerization catalysts, and have been used very effectively to help establish that the metal center is the true active site.

Another method for the synthesis of permanent zwitterionic polymerization catalysts is the substitution of one of the mono-anionic Cp ligands with a di-anionic ligand. This method was first examined by Jordan and co-workers³⁷ in 1989 with the use of the dianionic carboranyl ligand $[\text{C}_2\text{B}_9\text{H}_{11}]^{2-}$. The prepared compound, $[[\text{ZrCp}^*(\text{C}_2\text{B}_9\text{H}_{11})\text{Me}]_n]$ is polymeric, and only shows slight activity for olefins. Another system by Bercaw, Bazan, and coworkers³⁸ (Equation 1-4) contains an aminoborollide ligand, and although this system is not an active polymerization catalyst due to the



relatively electron-rich metal center, complexes using this ligand are likely to be developed into useful zwitterionic catalysts.

Other work on dianionic Cp ligands has been done by Bochmann and co-workers,³⁹ who developed Cp ligands containing Cp-B bonds. These ligands are prepared by the reaction of B(pfp)₃ with anionic Cp lithium reagents. The protonated Cp ligand can be deprotonated with alkyl lithium reagents and then metathesized onto group 4 metal complexes (Scheme 1-3). These systems are active polymerization catalysts; however, they are short-lived, probably owing to the relatively labile Cp-B bond, and they require the addition of a co-catalyst to become active.



Scheme 1-3

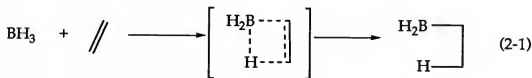
Considering the many potential benefits of zwitterionic olefin polymerization catalysts, we began to examine possible methods for preparing long-lived, stable zwitterionic catalysts by using tetraarylborates. Many methods were attempted, and the results of this study will be discussed.

CHAPTER 2

APPLICATION OF HYDROBORATION TO THE SYNTHESIS OF ZWITTERIONIC, GROUP 4 SINGLE-SITE POLYMERIZATION CATALYSTS

Introduction

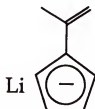
One of the most documented methods for the formation of a boron-carbon bond is the hydroboration reaction, pioneered by Brown and coworkers in the 1950s.⁴⁰ The general hydroboration process involves the reaction of a borane with an olefin, followed by hydride transfer through a



four-centered transition state (equation 2-1) The reaction proceeds according to Markovnikov's rule, with boron addition primarily at the least hindered carbon of the olefin. Considering the widespread use of this method for preparing B - C bonds and the relative ease of finding appropriate olefin and borane synthons, the utility of this method for synthesizing borate-containing metallocenes was examined.

In order to prepare a borate-containing metallocene using the hydroboration method, a cyclopentadienyl (Cp) ligand with a double bond must first be prepared. This can then react with a hydroborating agent that

will give good selectivity, and that can later be functionalized to form an anionic borate. Thus, the olefin synthon chosen was the α -methylvinylcyclopentadienyl ligand,⁴¹ which was first used by Rausch and



coworkers⁴² in the preparation of vinyl-substituted ferrocenes. This olefin was a useful candidate due to its ease of preparation, ease of forming metallocenes, and its 1,1-disubstitution. Brown and coworkers⁴³ have shown that 1,1-disubstituted olefins give the best specificity for Markovnikov addition, and the presence of the methyl group should also increase the electron density of the olefin, thus increasing its nucleophilicity.

The hydroborating agent used in this study, $\text{Ph}_2\text{BH}\cdot\text{Py}$, was initially synthesized by Hawthorne and coworkers,⁴⁴ and first used by Jacobs⁴⁵ as a hydroborating agent. $\text{Ph}_2\text{BH}\cdot\text{Py}$ is a useful hydroborating agent due to its relative stability towards oxygen and water and since it is relatively bulky, gives good selectivity according to Markovnikov's rule. The results of this study are discussed herein.

Experimental Section

General Considerations

All manipulations were performed under Ar by using standard Schlenk techniques or under N₂ in a Vacuum Atmospheres glove box. Glassware was oven dried prior to use. Solvents were distilled prior to use and stored over 4-Å molecular sieves in sealed bulbs under Ar. Diethyl ether and tetrahydrofuran were dried by distillation from Na/benzophenone ketyl. Pentane, hexanes, and toluene were dried by distillation from Na. NMR solvents were purchased from Cambridge Isotopes and were dried over 4-Å molecular sieves and not further purified. Pyridine was distilled prior to use. [Cp*RuCl]₄,⁴⁶ LiCp(C₃H₅),⁴² Ph₂BOMe,⁴⁴ Ph₂BH•Py,⁴⁵ Cp*CpZr(CH₃)₂,⁴⁷ and Cp*ZrCl₃⁴⁸ were prepared according to literature methods. α-Methylstyrene, CpTiCl₃, and 6,6-dimethylfulvene were purchased from Aldrich and used as received.

¹H NMR spectra were obtained by using either a Varian VXR-300, Gemini-300, or G.E. QE-300.

Procedures

Cp*RuCp(C₃H₅) (2-1). To a solution of [Cp*RuCl]₄ (0.20 g, 0.18 mmol) in 20 mL toluene was added a mixture of LiCp(C₃H₅) (0.08 g, 0.18 mmol) in 40 mL toluene and the reaction mixture was refluxed for 1 hour. The yellow mixture was filtered and the solvent was removed *in vacuo*. The yellow solid was extracted with hot hexanes, filtered through basic alumina, and the solvent removed *in vacuo* yielding 2-1 (0.15 g, 62 %) as an off-white solid. ¹H NMR (C₆D₆): δ 4.98 (t, 1H, CpC(CH₃)CH_aH_b), 4.84 (t, 1H, CpC(CH₃)CH_aH_b),

4.30 (t, 2H, Cp-H_a), 4.18 (t, 2H, Cp-H_b), 1.80 (s, 15H, Cp*), 1.73 (s, 3H, CpC(CH₃)CH_aH_b).

Cp*Zr(C₃H₅)Cl₂ (2-2). To a solution of Cp*ZrCl₃ (3.36 g, 10.1 mmol) in 30 mL toluene was added a solution of LiCp(C₃H₅) (1.20 g, 10.7 mmol) in 20 mL toluene. The reaction mixture was stirred for 20 hours and then refluxed for an additional three hours. The solvent was removed *in vacuo* and the resulting yellow solid was dissolved in 30 mL Et₂O and washed with 10 mL of H₂O. (Further manipulations were carried out in air.) The water layer was extracted twice with 10 mL Et₂O and the combined ether layer was dried over MgSO₄, filtered, and the solvent removed *in vacuo* to yield 2-2 (2.85 g, 70 %) as a yellow solid. ¹H NMR (C₆D₆): δ 6.10 (t, 2H, Cp-H_a), 5.50 (t, 2H, Cp-H_b), 5.35 (t, 1H, CpC(CH₃)CH_aH_b), 5.01 (t, 1H, CpC(CH₃)CH_aH_b), 2.05 (s, 3H, CpC(CH₃)CH_aH_b), 1.72 (s, 15H, Cp*).

Cp*Zr(C₃H₅)Cl₂ (2-3). To a solution of Cp*Zr(C₃H₅)Cl₂ (0.888 g, 2.20 mmol) in 20 mL Et₂O at -20 °C was added a solution of MeLi (3.20 mL, 4.48 mmol) in Et₂O over 30 minutes. The reaction mixture was warmed to 0 °C and the mixture was stirred for an additional 45 minutes before the mixture was warmed to room temperature. The mixture was stirred at room temperature for two hours, filtered, and the solvent removed *in vacuo* yielding 2-3 (0.61 g, 76 %) as a yellow solid. ¹H NMR (C₆D₆): δ 5.92 (t, 2H, Cp-H_a), 5.30 (t, 1H, CpC(CH₃)CH_aH_b), 5.25 (t, 2H, Cp-H_b), 4.96 (t, 1H, CpC(CH₃)CH_aH_b), 1.92 (s, 3H, CpC(CH₃)CH_aH_b), 1.63 (s, 15H, Cp*), -0.40 (s, 6H, Zr-Me₂).

CpZr(C₃H₅)Cl₂ (2-4). To a solution of CpTiCl₃ (0.39 g, 1.8 mmol) in 30 mL toluene was added a solution of LiCp(C₃H₅) (0.20 g, 1.8 mmol) in 20 mL toluene. The reaction mixture was stirred for 20 hours and then refluxed for an additional 20 hours. The solvent was removed *in vacuo* and the resulting

yellow solid was dissolved in 30 mL Et₂O and washed with 10 mL of H₂O. (Further manipulations were carried out in air.) The water layer was extracted twice with 10 mL Et₂O and the combined ether layer was dried over MgSO₄, filtered, and the solvent removed *in vacuo* to yield 2-4 (0.17 g, 30 %) as a yellow solid. ¹H NMR (C₆D₆): δ 6.10 (t, 2H, Cp-H_a), 5.97 (s, 5H, Cp), 5.77 (t, 2H, Cp-H_b), 5.15 (t, 1H, CpC(CH₃)CH_dH_b), 4.90 (t, 1H, CpC(CH₃)CH_aH_b), 1.80 (s, 3H, CpC(CH₃)CH_aH_b).

Reaction of Cp*RuCp(C₃H₅) with Ph₂BH•Py. To a solution of Cp*RuCp(C₃H₅) (0.083 g, 0.24 mmol) in 30 mL THF was added a solution of Ph₂BH•Py (0.062 g, 0.26 mmol) in 10 mL THF and the reaction mixture was stirred for 10 minutes. To this clear, colorless solution was added BF₃•OEt₂ (0.04 mL, 0.32 mmol) and the reaction mixture was stirred for an additional 5 hours. The reaction mixture was filtered and the solvent removed *in vacuo* yielding a yellow oil. The oil was triturated with Et₂O yielding a yellow solid. ¹H NMR in C₆D₆ indicated the product was a mixture of mostly Cp*RuCp(C₃H₇), and a small amount of unreacted Ph₂BH•Py.

Reaction of Cp*Cp(C₃H₅)ZrCl₂ with Ph₂BH•Py. To a solution of Cp*Cp(C₃H₅)ZrCl₂ (0.25 g, 0.62 mmol) in 30 mL THF was added a solution of Ph₂BH•Py (0.16 g, 0.65 mmol) in 10 mL THF. To this solution was added BF₃•OEt₂ (0.10 mL, 0.81 mmol) and the reaction mixture was stirred for 12 hours. The solvent was removed *in vacuo* and ¹H NMR in C₆D₆ indicated a mixture of starting material and new products, which were not discernible.

Reaction of Cp*Cp(C₃H₅)Zr(CH₃)₂ with Ph₂BH•Py. To a solution of Cp*Cp(C₃H₅)Zr(CH₃)₂ (0.15 g, 0.41 mmol) in 15 mL THF was added a solution of Ph₂BH•Py (0.10 g, 0.41 mmol) in 15 mL THF. To this solution was added BF₃•OEt₂ (0.05 mL, 0.41 mmol) and the reaction mixture was stirred for 36 hours. The solvent was removed *in vacuo* and the white solid was extracted

twice with 15 mL of pentane. The solvent was removed *in vacuo* yielding a white solid. ^1H NMR in C_6D_6 indicated a mixture of products, but complete conversion of starting material was observed by loss of Zr-CH_3 resonances. However, no loss of olefinic resonances was indicated.

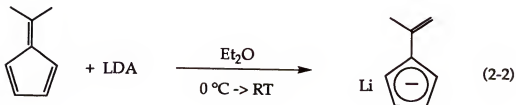
Reaction of $\text{Cp}^*\text{CpZr}(\text{CH}_3)_2$ with $\text{Ph}_2\text{BH}\cdot\text{Py}$. To a solution of $\text{Cp}^*\text{CpZr}(\text{CH}_3)_2$ (0.55 g, 1.7 mmol) in 25 mL THF was added a solution of $\text{Ph}_2\text{BH}\cdot\text{Py}$ (0.44 g, 1.8 mmol) in 15 mL THF. To this solution was added $\text{BF}_3\cdot\text{OEt}_2$ (0.22 mL, 1.8 mmol) and the reaction mixture was stirred for 24 hours. The solvent was removed *in vacuo* and the white solid was extracted twice with 15 mL of pentane. Removal of solvent yielded a white solid.

^1H NMR (C_6D_6): δ 8.05 (d, 2H), 7.50 (d, 2H), 7.32 (t, 4H), 7.21 (t, 4H), 6.49 (t, 1H), 6.10 (t, 2H), 5.96 (s, 5H), 1.85 (s, 15H).

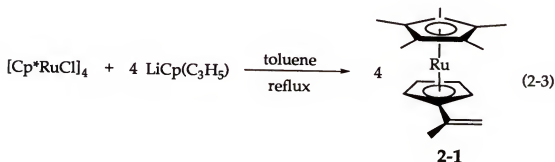
Results and Discussion

Syntheses.

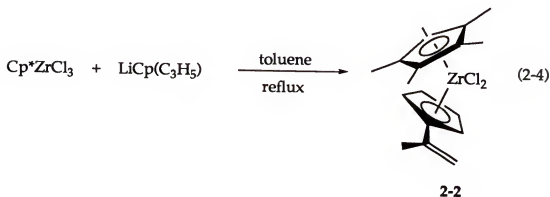
Preparation of the ligand was performed according to the procedure of Rausch and coworkers.⁴² Addition of lithium diisopropylamide (LDA) to a solution of 6,6'-dimethylfulvene in diethyl ether yields the deprotonated $\text{LiCp}(\text{C}_3\text{H}_5)$ product in high yield (equation 2-2), which is best



described as a pseudo-enolate salt. Once the salt is prepared, a number of metallocenes can be prepared. Our initial studies examined the formation of the ruthenocene **2-1**, which is prepared by the reaction of four equivalents of the anionic Cp ligand with the $[\text{Cp}^*\text{RuCl}]_4$ tetramer in refluxing toluene (equation 2-3).

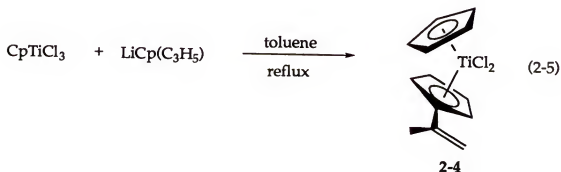


The syntheses of **2-2** and **2-4** were accomplished *via* similar methods utilizing the metathetical reaction of Cp^*ZrCl_3 or Cp^*TiCl_3 respectively, with

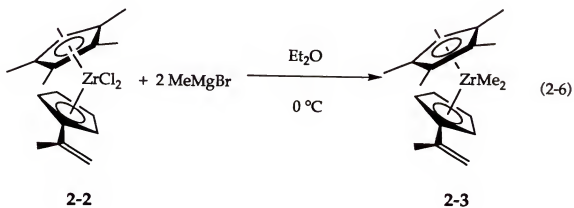


LiCpC_3H_5 in toluene. Thus, **2-2** was prepared by the reaction of Cp^*ZrCl_3 with LiCpC_3H_5 (equation 2-4), and the reaction was stirred for 20 hours. Since reaction was incomplete after that time, the mixture was refluxed for an

additional three hours. Workup of the product by standard methods⁴⁹ gave the product in good yields. A similar procedure was followed for **2-4**, and the reaction of CpTiCl_3 with LiCpC_3H_5 yielded **2-4** after standard workup (equation 2-5). However the reaction required an additional 20 hours of reflux for the reaction to go to completion, and the yield was still relatively low.

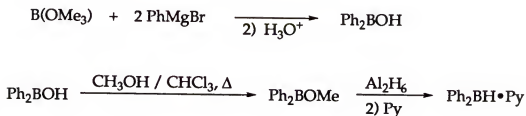


The dimethyl zirconocene **2-3** was prepared according to standard methods,⁵⁰ and addition of two equivalents of MeMgBr to the zirconocene dichloride **2-2**, in ether, yielded **2-3** in good yield (equation 2-6).



Hydroboration Reactions.

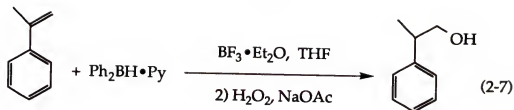
The hydroborating agent, $\text{Ph}_2\text{BH}\cdot\text{Py}$ was prepared according to the procedure by Jacobs (scheme 2-1) in which trimethoxyborane is allowed to react with two equivalents of PhMgBr . Hydrolysis of the reaction mixture and separation of the ether layer gives Ph_2BOH . Ph_2BOMe can be obtained by azeotropic distillation of the boric acid with methanol and chloroform. Finally the borane product can be obtained by reduction of the methoxide



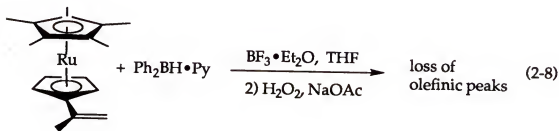
Scheme 2-1. Synthesis of $\text{Ph}_2\text{BH}\cdot\text{Py}$

with alane, prepared *in situ* by the reaction of 100% sulfuric acid with LiAlH_4 . Addition of pyridine during the last step produces the protected borane product which is stable to both oxygen and water.

To examine the ability of the relatively bulky borane to hydroborate a 1,1-disubstituted olefin, we attempted the hydroboration of the analogous α -methylstyrene and isolated the appropriate alcohol after oxidation by standard methods (equation 2-7). Therefore, we concluded that the relatively bulky borane was indeed reactive with the slightly hindered 1,1-disubstituted olefin.



To further model the chemistry of the hydroboration process, $\text{Ph}_2\text{BH}\cdot\text{Py}$ was reacted with **2-1** and isolation of the hydroboration product was attempted. For $\text{Ph}_2\text{BH}\cdot\text{Py}$ to act as a hydroborating agent, the coordinated pyridine must first be removed, and this is accomplished using the stronger Lewis acid, $\text{BF}_3\cdot\text{OEt}_2$. Nucleophilic attack by the olefin can then occur at the activated borane yielding the hydroboration product. Initial ^1H NMR studies



of the product, after workup, showed complete loss of the olefinic protons (equation 2-8), indicating the expected hydroboration process had occurred. However, integration of the remaining resonances indicated that a full equivalent of borane was not present and the aromatic resonances were due to unreacted borane starting material. Further investigation of the spectrum indicated that the product was actually the symmetrical, $\text{Cp}^*\text{RuCp}(\text{C}_3\text{H}_7)$ (**B**), (Figure 2-1) which was indicated by a doublet at 1.08 ppm (H^a) which integrated to 6 protons and a symmetric multiplet at 2.35 ppm which

integrated to 1 proton (H^b). This pattern is indicative of an isopropyl group, and the absence of a methylene resonance (H^c) also ruled out structure A.

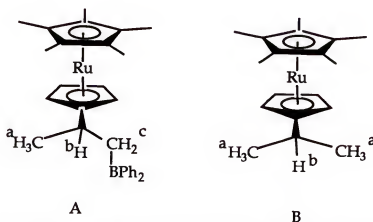
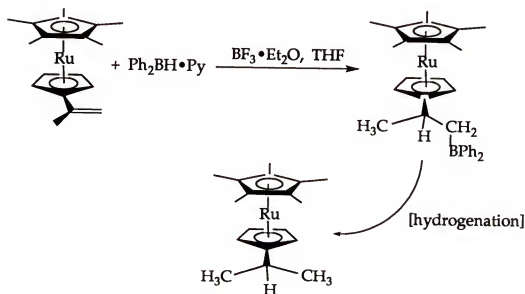


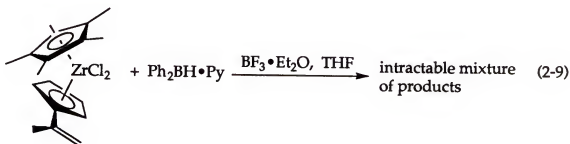
Figure 1. Structure of anticipated hydroboration product (A), and structure of isolated product (B).



Scheme 2. Probable method for the formation of the observed hydroboration product.

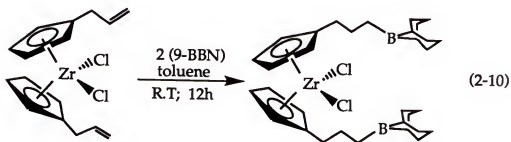
Although this was not an anticipated product, a likely mechanism for the formation of the isopropyl group involves hydroboration of the olefin, followed by hydrogenation of the trialkylborane product (scheme 2). This conversion of olefins to saturated hydrocarbons through hydroborating agents has not, to our knowledge, been previously described, however we chose not to continue examination of the mechanism. Considering that the only plausible method of getting a saturated hydrocarbon from the initial olefin involves the initial hydroboration of the olefin, we decided to proceed with the examination of the group 4 systems.

Initial studies of the group 4 systems involved the zirconocene dichloride complex 2-2 (equation 2-9). The reactions were carried out in THF with one equivalent each of 2-2, $\text{Ph}_2\text{BH}\cdot\text{Py}$, and $\text{BF}_3\cdot\text{OEt}_2$. The reaction temperatures were systematically altered from room temperature, in which no reaction occurred, to refluxing THF, in which only partial conversion was attained. Even after refluxing in THF for 2 days, conversion was not complete, and the resulting mixture of starting materials and products could not be separated or fully identified.

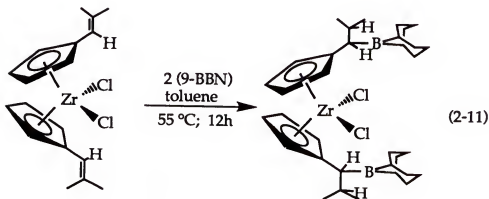


Similar results were obtained by Erker and Aul working with related compounds. They observed that the hydroboration reaction was indeed

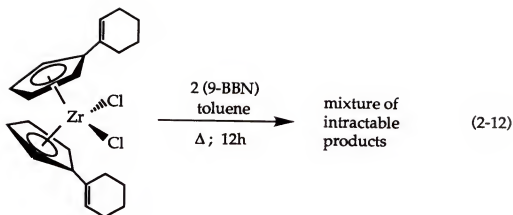
possible with Group 4 metallocene dichlorides, and when borabicyclo[3.3.0]nonane (9-BBN) was allowed to react with bis(allyl-Cp)zirconium dichloride (equation 2-10), the reaction was facile at room



temperature. However, hydroborating the bis(vinyl-Cp)zirconium dichloride with 9-BBN required greater temperatures and the product yield was less (equation 2-11).

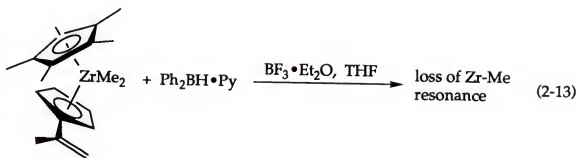


Furthermore, when there was a substituent present in the α -position of the vinyl-Cp complexes (equation 2-12), no reaction of the olefin occurred, and the resulting mixtures of organometallics could not be identified.

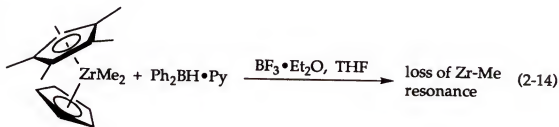


It can be concluded from our results and those of Erker, that the reason for the low reactivity of **2-2** is likely due to a combination of both electronic and steric effects. When the olefin moiety is in resonance with the aromatic Cp ring, the reactivity of the olefin is decreased toward hydroboration. This can be explained by considering that the high oxidation state of the metal center draws the π -electron density away from the Cp ring and thus through resonance, reduces the electron density within the olefin. The reactivity is decreased even more by the presence of an α -substituent on the vinyl group. It is likely that the steric interactions caused by the additional substituent, in addition to the electronic disadvantages, is too great of a barrier for the hydroboration reaction to be applicable, and other side reactions predominate.

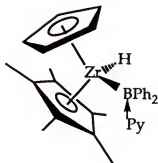
Similar studies were conducted on the dimethyl zirconocene **2-3**, and hydroboration of the olefin was again not possible. However other reactivity was observed which was unexpected. When **2-3** was reacted with $\text{Ph}_2\text{BH}\cdot\text{Py}$ and $\text{BF}_3\cdot\text{OEt}_2$ in THF, a reaction was observed and all starting material was consumed in the reaction. This was indicated by complete loss of the Zr-CH_3 resonance, which in the starting material appears at -0.40 ppm, and the



appearance of new olefinic and Cp resonances. To determine if the olefin was involved in the reaction, a similar reaction was attempted with $\text{Cp}^*\text{CpZr}(\text{CH}_3)_2$ under the same reaction conditions. Again, a new Cp resonance was observed and the Zr-CH₃ resonance was completely lost.



Integration of the spectrum was consistent with loss of the two methyl groups and addition of $\text{Ph}_2\text{BH}\cdot\text{Py}$. Therefore, the following structure was proposed. Unfortunately, the sample slowly decomposed at room temperature under a nitrogen atmosphere, and additional studies could not be accomplished.



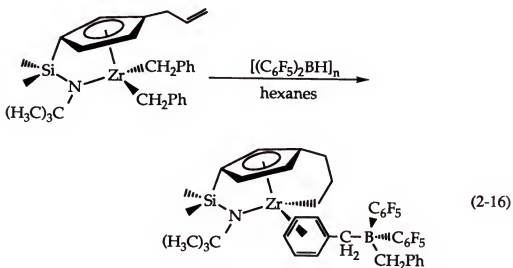
Related work by Marks⁵² and Hartwig⁵³ and their coworkers lend support to the proposed structure. Marks reports the organolanthanide-catalyzed hydroboration of olefins with catecholborane and a bulky alkyl decamethylanthracene. In this study, a lanthanum - alkyl bond is exchanged with a boron - hydride bond, leading to a lanthanum hydride and boron alkyl. More closely related is the work by Hartwig and coworkers, who discuss the synthesis of early transition metal boryl and hydridoboryl complexes. They report that the reaction of catecholborane with Cp_2NbH_3 leads to the loss of H_2 and the formation of the borylniobocene. The niobocene structure is supported by a crystal structure in which all atoms were found, including the hydrides.



Conclusions.

Hydroboration is a well documented method for preparing B - C bonds, and the reaction is clearly understood. With early transition metal systems however, hydroboration is not a useful method for preparing borate-

containing metal complexes. The problem with this method stems from the relatively high reactivity of the boron - alkyl bond which is susceptible to cleavage by interaction with the metal center. Similarly, the highly reactive boron - hydride bond can also interact with the metal center, leading to intractable mixtures of products. A recent study by Spence and Piers⁵⁴ displays the benefits and disadvantages of using hydroboration with group 4 metal complexes. In their study, they examined the hydroboration of 2-propenyl substituted Cp ligands on zirconocenes and found that hydroboration was possible with the perfluorinated diphenylborane. However, further reactivity was observed including cleavage of the boron-alkyl bond, formation of a new zirconium - alkyl bond, and formation of a new boron - alkyl bond.



Clearly, this demonstrates the usefulness of hydroboration for forming a borane-containing metal complex. However, the susceptibility of the boron - alkyl bond to cleavage by interaction with the metal center is also obvious.

CHAPTER 3 SYNTHESIS, CHARACTERIZATION, AND STRUCTURE OF NOVEL BORANE- AND BORATE-CONTAINING RUTHENOCENES

Introduction

The development of weakly-coordinating anions (WCA) has been of increasing interest in recent years because of their usefulness in a wide variety of chemical applications. The diversity of WCA spans the classical anions ClO_4^- , SO_3CF_3^- , BF_4^- , PF_6^- , and SbF_6^- to the even more weakly coordinating anions BPh_4^- , $\text{CB}_{11}\text{H}_{12}^-$, C_{60}^- , and methylalumoxane (MAO).⁵⁵ Tetraarylborates have been extensively used in electrolytes,⁵⁶ as phase-transfer catalysts,⁵⁷ and as WCA for group 4 polymerization catalysts,⁵⁸ Rh(I) hydride hydrogenation complexes,⁵⁹ and thousands of other transition metal complexes.⁵⁵ Fluorinated tetraphenylborates are among the most weakly-coordinating anions known, and tetrakis[3,5-bis(trifluoromethyl)phenyl]borate⁵⁷ (TFPB) and tetrakis(perfluorophenyl)borate^{58d} have been used as counter-ions for late transition-metal catalyst systems⁶⁰ as well as highly active group 4 polymerization catalysts.⁵⁸ Recently, Marks and coworkers⁶¹ developed an even bulkier anion, tetrakis(*p*-trimethylsilyl-tetrafluorophenyl)borate, for use in these systems.

Several examples of borates bound to metal complexes through both σ and π interactions have been reported.^{62,63} Bochmann and coworkers⁶⁴ reported the syntheses of novel anionic and zwitterionic group 4 metallocene complexes by employing the (cyclopentadienyl)-tris(perfluorophenyl)borate

ligand. These complexes exhibit moderate activity toward olefin polymerization, although the metal center must still be activated by addition of a cocatalyst (i.e., AlMe_3). Under some conditions, the ligand systems displayed loss of borane and decomposition, which may be due to an associated / dissociated boron equilibrium process.⁶⁵ Other examples of cyclopentadienyl (Cp) ligands containing tethered boranes have been synthesized by hydroboration⁶⁶ and other methods,⁶⁷ but to our knowledge, no Cp ligands with tethered borates have been reported.

Tetraphenylborates have also been used as ligands through η^6 -coordination of a phenyl group to a multitude of metal centers,⁵⁵ including various group 4 metal complexes.⁶⁸ These group 4 zwitterionic complexes are active polymerization catalysts; however, the dissociation of the borate ligand to form an ion pair precedes the coordination of olefin. Given the instability of the known σ -bound borates and the impermanent nature of the π -bound borates, we have prepared borate-containing cyclopentadienyl (Cp) ligands in which the boron is not bound directly to the Cp ring. For initial applications of the new tethered-borate ligands, we have chosen to synthesize ruthenocene derivatives.

During the past several years, a number of new cyclopentadienyl ligands have been synthesized and characterized with the pentamethylcyclopentadienylruthenium(II) (Cp^*Ru) moiety as a template.⁶⁹ The benefits of using the Cp^*Ru moiety are many. It allows for the simple high-yield synthesis of stable ruthenocenes from the readily accessible $[\text{Cp}^*\text{RuCl}]_4$ tetramer. Since the Cp^*Ru moiety is held constant, the electronic and steric properties of the new ligand can be compared with other ligands. The oxidation properties of many ruthenocenes have been studied, and the nature of the counter-ion plays an important role in the oxidation process.

For example, TFPB, when used⁵⁶ as an electrolyte in the electrochemical oxidation studies of osmocene and ruthenocene, leads to a quasi-reversible single-electron ruthenium(II/III) electrochemical couple. (In common solvent/electrolyte systems, osmocene⁷⁰ exhibits an irreversible one-electron oxidation, and ruthenocene⁷⁰ exhibits an irreversible two-electron oxidation.) Therefore, we sought to produce ruthenocenes containing tethered borates and investigate the effect of the borate-containing ligand on the oxidation chemistry of the resultant ruthenocenes.

Experimental Section

General Considerations

All manipulations were performed under Ar by using standard Schlenk techniques or under N₂ in a Vacuum Atmospheres glove box. Glassware was oven dried prior to use. Solvents were distilled prior to use and stored over 4-Å molecular sieves in sealed bulbs under Ar. Diethyl ether and tetrahydrofuran were dried by distillation from Na/benzophenone ketyl. Pentane was dried by distillation from Na. NMR solvents were purchased from Cambridge Isotopes and were dried over 4-Å molecular sieves and not further purified. Pyridine was distilled prior to use. [Cp^{*}RuCl]₄⁷¹ and Ph₂BOMe⁷² were prepared according to literature methods. *p*-Diiodobenzene, *p*-dibromobenzene, 6,6-dimethylfulvene, and BuLi (2.5M in hexanes) were purchased from Aldrich and used as received.

¹H and ¹³C NMR spectra were obtained by using either a Varian VXR-300, Gemini-300, or G.E. QE-300. Mass Spectra were obtained with a FinniganMAT MAT95Q Liquid Secondary Ion Mass Spectrometer (LSI MS, Cs⁺); the selected (*m*+1)/*z* values given refer to the isotopes ¹H, ¹²C, ⁷⁹Br, ¹²⁷I,

^{11}B , and ^{101}Ru . Elemental Analyses were obtained by the microanalytical department at the University of Florida.

Procedures

LiCpC(CH₃)₂PhBr (3-1). To a solution of *p*-dibromobenzene (3.00 g, 12.7 mmol) in 150 mL Et₂O at -78 °C was added BuLi (5.10 mL, 12.7 mmol). The mixture was allowed to warm to room temperature over 30 min. To this solution was added 6,6-dimethylfulvene (1.54 g, 14.5 mmol) *via* syringe, and white solid precipitated immediately. The mixture was stirred for 2 h at 25 °C and then filtered. The white solid was washed with 3 x 20 mL pentane and then dried *in vacuo* yielding 3.20 g (92.3 % yield) of **3-1** as a white solid. ^1H NMR (C₆D₆/CD₃CN) δ 7.20 (s, 4H), 5.85 (t, 2H), 5.73 (t, 2H), 1.67 (s, 6H). ^{13}C NMR (C₆D₆/CD₃CN) δ 153.74, 130.73, 129.82, 128.88, 118.57, 102.72, 102.25, 39.49, 32.01.

LiCpC(CH₃)₂PhI (3-2). To a solution of *p*-diiodobenzene (3.01 g, 9.10 mmol) in 150 mL Et₂O at -78 °C was added BuLi (3.64 mL, 9.10 mmol). The mixture was allowed to warm to room temperature over 30 min. To this solution was added 6,6-dimethylfulvene (1.10 g, 9.13 mmol) *via* syringe, and white solid precipitated immediately. The mixture was stirred for 2 h at 25 °C and then filtered. The white solid was washed with 3 x 20 mL pentane and then dried *in vacuo* yielding 2.62 g (91.2 % yield) of **3-2** as a white solid. ^1H NMR (C₆D₆/CD₃CN) δ 7.40 (d, 2H), 7.10 (d, 2H), 5.72 (t, 2H), 5.63 (t, 2H), 1.67 (s, 6H). ^{13}C NMR (C₆D₆/CD₃CN) δ 154.78, 137.73, 129.64, 129.24, 102.47, 102.08, 89.76, 39.60, 32.03.

Cp^{*}RuCpC(CH₃)₂PhBr (3-3). To a mixture of [Cp^{*}RuCl]₄ (0.51 g, 0.47 mmol) and **1** (0.50 g, 1.85 mmol) was added 15 mL THF, and the reddish solution was refluxed for 10 hours. The THF was then pumped away, and 5 g

basic alumina added. The mixture was extracted twice with 20 mL hot hexanes, and the slightly yellow solution was evaporated to yield 3-3 (0.79 g, 85 % yield) as an off-white solid. Needle-like, X-ray quality crystals were obtained by cooling a concentrated solution of 3-3 in hot hexanes.

Anal. Calcd for $C_{24}H_{29}BrRu$: C, 57.81, H, 5.86. Found: C, 57.66, H, 5.98.

LSI MS: $(m+1)/z$ Calculated, 498. Found 498. ^1H NMR (C_6D_6) δ 7.24 (d, 2H), 7.01 (d, 2H), 4.11 (t, 2H), 4.00 (t, 2H), 1.88 (s, 15H), 1.41 (s, 6H). ^{13}C NMR (C_6D_6) δ 151.30, 131.12, 127.84, 126.22, 88.00, 84.96, 73.17, 71.29, 37.96, 29.94, 12.31.

Cp* Ru CpC(CH₃)₂PhI (3-4). To a mixture of [Cp* Ru Cl]₄ (0.66 g, 2.44 mmol) and 3-2 (0.77 g, 2.44 mmol) was added 15 mL THF, and the reddish solution was refluxed for 10 hours. The THF was then pumped away, and 5 g basic alumina added. The mixture was dissolved in 20 mL hot hexanes, filtered and the solid washed again with 20 mL hot hexanes. The slightly yellow solution was evaporated to yield 3-4 (1.02 g, 77 % yield) as an off-white solid. Recrystallization from hexanes yielded yellow needle-like crystals.

Anal. Calcd for $C_{24}H_{29}IRu$: C, 52.81, H, 5.36. Found C, 53.89, H, 5.61.

LSI MS: $(m+1)/z$ Calculated, 546. Found 546. ^1H NMR (C_6D_6) δ 7.43 (d, 2H), 6.89 (d, 2H), 4.11 (t, 2H), 4.00 (t, 2H), 1.88 (s, 15H), 1.41 (s, 6H). ^{13}C NMR (C_6D_6) δ 151.48, 137.23, 128.74, 103.84, 91.04, 84.99, 73.20, 71.32, 38.05, 29.89, 12.42.

Cp* Ru CpC(CH₃)₂PhBPh₂-Py (3-5). To a solution of 3-3 (0.16 g, 0.59 mmol) in 20 mL Et₂O at -78 °C was added BuLi (0.13 mL, 0.59 mmol), and the solution was warmed to room temperature over 30 min. To this solution was added Ph₂BOMe (0.064 mL, 0.59 mmol) via syringe. The solution stirred for seven hours by which time white solid had precipitated. The solvent was removed *in vacuo*, and the solid was extracted twice with 10 mL hot hexanes. The solution was concentrated to 5 mL, and then pyridine (0.05 mL) was added *via* syringe. The solid that formed was filtered and washed with 5 mL

hexanes and then dried *in vacuo* yielding **3-5** (0.15 g, 71 % yield) as a white solid. Recrystallization from THF/hexanes yielded crystals suitable for X-ray diffraction studies. ^1H NMR ($\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$) δ 8.24 (m, 6H), 7.52-7.16 (m, 14H), 6.54 (br t, 2H), 6.10 (br t, 2H), 4.30 (t, 2H), 4.02 (t, 2H), 1.90 (s, 15H), 1.65 (s, 6H). ^{13}C NMR ($\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$) δ 151.42, 134.77, 134.63, 127.56, 125.17, 124.94, 123.56, 105.41, 84.32, 72.52, 71.24, 37.57, 29.85, 11.95.

Cp* $\text{RuCpC}(\text{CH}_3)_2\text{PhBPh}_3\text{Li}(\text{Et}_2\text{O})_{1/2}$ (3-6a**).** To a solution of **3-3** (0.50 g, 1.0 mmol) in 20 mL Et_2O at -78°C was added BuLi (0.40 mL, 1.0 mmol), and the solution was warmed to room temperature over 30 min. To this solution was added BPh_3 (0.24 g, 1.0 mmol). A white solid precipitated immediately, and the mixture was stirred for one additional hour. The solid was filtered, washed twice with 5 mL hexanes, and then dried *in vacuo* yielding **3-6a** (0.47 g, 70% yield) as a white solid. Recrystallization from cold THF/hexanes yielded crystals suitable for X-ray diffraction studies. ^1H NMR ($\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$) δ 7.86 (m, 6H), 7.76 (m, 2H), 7.10 (t, 8H), 7.08 (t, 3H), 4.33 (t, 2H), 4.01 (t, 2H), 3.25 (q, 2H), 1.93 (s, 15H), 1.66 (s, 6H), 1.10 (t, 3H). LSI MS (for anion): m/z Calculated, 661. Found 661.

NMR data for **3-6**. ^1H NMR ($\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$) δ 7.58 (m, 6H), 7.44 (m, 2H), 7.03 (t, 8H), 6.85 (t, 3H), 4.17 (t, 2H), 3.89 (t, 2H), 1.83 (s, 15H), 1.49 (s, 6H). ^{13}C NMR ($\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$) δ 151.33, 137.04, 136.33, 135.80, 125.60, 123.40, 121.64, 84.61, 72.41, 71.79, 38.20, 30.62, 12.39.

X-ray Structural Analysis of 3-3. Data were collected at 173 K on a Siemens SMART PLATFORM equipped with A CCD area detector and a graphite monochromator utilizing $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Cell parameters were refined using up to 8192 reflections. A hemisphere of data (1381 frames) was collected using the ω -scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor

instrument and crystal stability (maximum correction on I was < 1 %). Psi scan absorption corrections were applied based on the entire data set.

The structure was solved by the Direct Methods in SHELXTL5⁷³ and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. 236 parameters were refined in the final cycle of refinement using 4472 reflections with $I > 2\sigma(I)$ to yield R1 and $\omega R2$ of 0.0326 and 0.075 , respectively. Refinement was done using F2.

X-ray Structural Analysis of 3-6b. Data were collected at 173 K on a Siemens SMART PLATFORM equipped with A CCD area detector and a graphite monochromator utilizing MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Cell parameters were refined using up to 8192 reflections. A hemisphere of data (1381 frames) was collected using the ω -scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1 %). Psi scan absorption corrections were applied based on the entire data set.

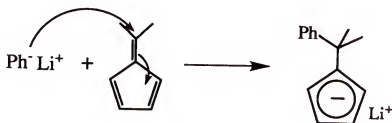
The structure was solved by the Direct Methods in SHELXTL5⁷³ and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. The four THF ligands around the Li atom are disordered over eight positions with site occupation factors of one set being 0.51(3), 0.56(1), 0.70(2) and 0.52(1) with the other four parts having occupation factors of the complement to 1.0. The oxygen atoms of each THF molecule were not disordered. 735 parameters were refined in the final cycle of refinement using 7092 reflections with $I >$

2 σ (I) to yield R1 and ω R2 of 0.045 and 0.0989 , respectively. Refinement was done using F2.

Results and Discussion

Syntheses

The use of 6,6-dimethylfulvene to prepare anionic Cp-ligands has been previously demonstrated in preparing both non-bridged⁷⁴ and bridged⁷⁵ metallocenes. The usefulness of this precursor arises from the exclusive addition of a nucleophile at the exocyclic carbon,^{74d} leading to anionic Cp salts that are unable to undergo Diels-Alder dimerizations.

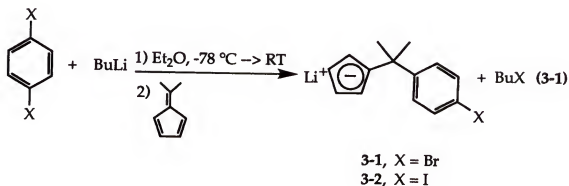


Precipitation of the lithium salt allows for the convenient and simple isolation of the product by filtration from a relatively non-polar solvent (diethyl ether).

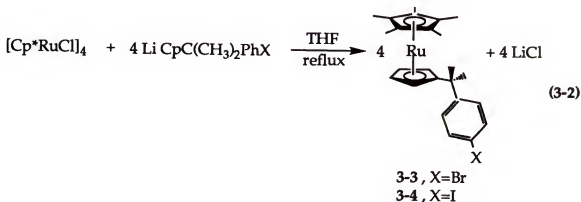
Para-substituted dihalobenzenes undergo mono-lithiation reactions via the halo-lithium exchange⁷⁶ process leading to a nucleophilic carbanion. Thus, using both dibromo- and diiodobenzene with 6,6-dimethylfulvene as synthons, we have developed a new class of derivatizable Cp ligands.

The addition of one equivalent of BuLi to a solution of *p*-dibromobenzene in diethyl ether leads to the formation of *p*-

bromophenyllithium. The slow addition of one equivalent of 6,6-dimethylfulvene to this solution quickly forms the desired lithium salt $\text{LiCpC}(\text{CH}_3)_2\text{PhBr}$ (**3-1**), which precipitates as a white solid (eq 3-1). Similarly, $\text{LiCpC}(\text{CH}_3)_2\text{PhI}$ (**3-2**) is prepared in the same way by using *p*-diiodobenzene.

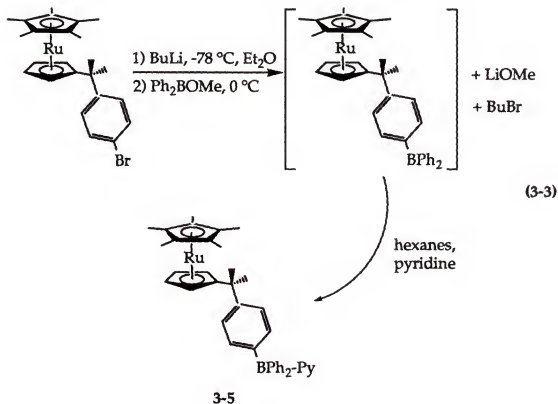


If a mixture of one equivalent of $[\text{Cp}^*\text{RuCl}]_4$ and four equivalents of **3-1** in THF is refluxed for 10 hours, the $\text{Cp}^*\text{RuCpC}(\text{CH}_3)_2\text{PhBr}$ product (**3-3**) is isolated in good yield after standard work-up⁷¹ (eq 3-2). Similarly, the iodo-ruthenocene (**3-4**) is prepared by using $[\text{Cp}^*\text{RuCl}]_4$ and **3-2**. Both ruthenocenes are easily crystallized, and X-ray quality crystals are obtained by

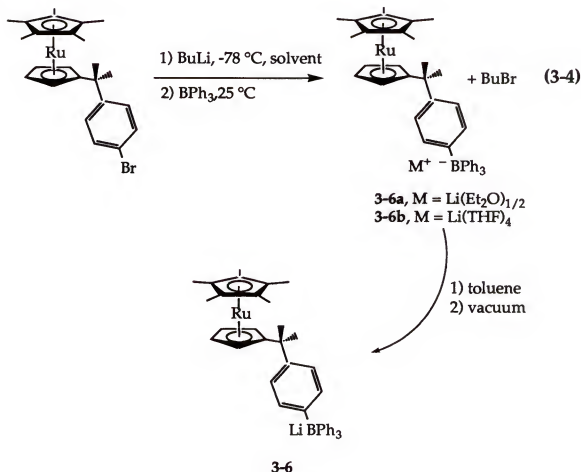


cooling a hot hexanes solution of the appropriate ruthenocene. These ruthenocenes are air-stable and can be manipulated without any precautions.

Boron-containing derivatives have been synthesized from the bromo-ruthenocene precursor 3-3. The addition of BuLi to a solution of 3-3 in Et₂O forms the phenyl lithiate, which can be trapped by the addition of Ph₂BOMe (eq 3-3). Addition of pyridine leads to the insoluble pyridine adduct (3-5), which can be recrystallized from THF/hexanes. Unfortunately, solvent molecules present in the crystal contributed substantial disorder, and an anisotropically refined structure could not be obtained. Similarly, the presence of solvent made it difficult to obtain a precise chemical analysis. However the NMR data, preliminary structure, and elemental analysis clearly indicate the formation of the desired neutral complex.



The addition of BuLi to **3-3** in Et₂O, followed by the addition of triphenylboron, leads to the formation of the borate-ruthenocene **3-6a** as a lithium-etherate salt (eq 3-4). When the reaction is run in THF at -78° C, the borate product remains soluble and the solvent must be removed *in vacuo*. The product (**3-6b**) is isolated as a Li(THF)₄ salt. The base-free salt (**3-6**) is prepared by stripping the diethyl ether from **3-6a** by suspending the solid in benzene or toluene and then removing the solvent under vacuum (eq 3-4).



The reaction of the lithiated ruthenocene with the perfluorinated triphenylborane, B(C₆F₅)₃, was also attempted, and the anticipated product

was observed by ^1H NMR spectroscopy. However, attempts to isolate the product proved difficult due to the similar solubilities of the ruthenocene-borate and undesirable side-products.

NMR studies

All products were characterized by both ^1H NMR and ^{13}C NMR. In **3-1**, the Cp protons are at 5.73 ppm and 5.85 ppm. The signals are tight triplets similar to that observed^{74a} for most mono-substituted Cp ligands. The two phenyl resonances, which typically are two doublets, overlap in one broadened singlet. The overlap in the chemical shifts is a result⁷⁷ of similar effects on both the ortho- and meta-position by the Br substituent. The ^1H NMR spectrum of **3-2** is similar to **3-1**, except that the phenyl region is cleanly split as two doublets, with the resonance for the proton ortho to the iodide further downfield.

The ^1H NMR spectra of the three neutral ruthenocenes, **3-3**, **3-4**, and **3-5**, can be compared to examine the effects of the substitution on the molecular and electronic structure of the metal complexes. The spectra of compounds **3-3** and **3-4** show that altering the halogen on the phenyl group affects the electronics of the ring but has little or no effect on the ruthenocene moiety of the complex. As in the NMR spectra of the free ligands **3-1** and **3-2**, the iodo-substituent has a much greater effect on the ortho and meta resonances (7.42 ppm and 6.90 ppm respectively) versus the bromo-substituent (7.23 ppm and 7.02 ppm). However, all other chemical shifts of the protons within the three molecules are identical. This similarity indicates that the sp^3 carbon bridging the Cp and the phenyl group prevents significant intra-ligand electronic effects at the metal by the substituted phenyl group.

The ^1H NMR spectrum of **3-5** is comparable to that of the bromo- and iodo-ruthenocenes, but with a few minor differences. The chemical shift of the Cp^* protons is at 1.88 ppm, which is identical to the two other neutral ruthenocenes. However, the chemical shift of the terminal methyl protons of the bridging carbon is at 1.65 ppm, which is shifted downfield 0.23 ppm from the halo-ruthenocenes. Likewise, there is a small difference in the Cp protons which are at 4.02 ppm and 4.41 ppm, as compared to 3.99 ppm and 4.11 ppm for the halo-ruthenocenes. The aromatic region clearly indicates the presence of a coordinated pyridine ligand with broadened triplets at 6.09 ppm (meta) and 6.55 ppm (para), and a broadened doublet at 8.23 ppm (ortho). The phenyl region displays unresolvable overlapping signals.

The ^1H NMR spectrum of **3-6** displays a characteristic splitting pattern for the protons ortho to the borate. These signals come downfield of the normal aromatic region (7.44 ppm and 7.58 ppm), and the splitting patterns are complex. The signal observed for protons ortho to the boron has a characteristic symmetrical seven-line pattern similar to other *p*-substituted phenyl borates observed in our lab. The Cp resonances are at 3.89 ppm and 4.17 ppm, and are more broadly split than in the neutral ruthenocenes, possibly due to the orientation of the counterion. The Cp^* resonances and terminal methyl resonances are at 1.83 ppm and 1.49 ppm respectively, which are similar to those of the equivalent protons in the neutral ruthenocenes.

The ^1H NMR spectrum of the diethyl etherate **3-7** is slightly different than the non-solvated salt **3-6** only in that all corresponding resonances are shifted down-field, although by varying amounts.

Table 3-1. Crystal data and structure refinement for 3-3.

Empirical formula	C ₂₄ H ₂₉ Br Ru
Formula weight	498.45
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 10.3587(1) Å α = 90° b = 24.9529(2) Å β = 99.030(1)° c = 8.3765(1) Å γ = 90°
Volume, Z	2138.34(4) Å ³ , 4
Density (calculated)	1.548 Mg/m ³
Absorption coefficient	2.607 mm ⁻¹
R(000)	1008
Crystal size	0.22 x 0.28 x 0.34 mm
Theta range for data collection	1.63 to 27.50 deg.
Limiting indices	-14 ≤ h ≤ 14, -33 ≤ k ≤ 16, -11 ≤ l ≤ 7
Reflections collected	11687
Independent reflections	4875 [R(int) = 0.0326]
Absorption correction	Integration, SHELXTL
Max. and min. transmission	0.6002 and 0.4621
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4836 / 0 / 236
Goodness-of-fit on F ²	1.175
Final R indices [I > 2σ(I)]	R1 = 0.0326, wR2 = 0.0750
R indices (all data)	R1 = 0.0378, wR2 = 0.0816
Extinction coefficient	0.00062(14)
Largest diff. peak and hole	0.530 and -0.550 e.Å ⁻³

Table 3-2. Crystal data and structure refinement for **3-6b**.

Empirical formula	C ₅₈ H ₇₆ B Li O ₄ Ru
Formula weight	956.01
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pbcn
Unit cell dimensions	a = 40.9162(6) Å $\alpha = 90^\circ$ b = 14.4443(3) Å $\beta = 90^\circ$ c = 17.6316(3) Å $\gamma = 90^\circ$
Volume, Z	10420.4(3) Å ³ , 8
Density (calculated)	1.219 Mg/m ³
Absorption coefficient	0.345 mm ⁻¹
R(00)	4064
Crystal size	0.32 × 0.25 × 0.18 mm
Theta range for data collection	1.50 to 25.00 deg.
Limiting indices	-53 ≤ h ≤ 50, -16 ≤ k ≤ 18, -22 ≤ l ≤ 24
Reflections collected	53780
Independent reflections	9167 [R(int) = 0.0490]
Absorption correction	Integration, SHELXTL
Max. and min. transmission	0.949 and 0.748
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	9069 / 202 / 735
Goodness-of-fit on F ²	1.135
Final R indices [I > 2σ(I)]	R1 = 0.0450, wR2 = 0.0989
R indices (all data)	R1 = 0.0663, wR2 = 0.1180
Extinction coefficient	0.00000(4)
Largest diff. peak and hole	0.488 and -0.747 e.Å ⁻³

Table 3-3. Selected Bond Lengths and Angles for $\text{Cp}^*\text{RuCpC}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{Br}(3-3)$.

Bond Distances (Å)			
Ru - C1	2.199 (3)	Ru - C6	2.213 (3)
Ru - C2	2.178 (3)	Ru - C7	2.189 (3)
Ru - C3	2.171 (3)	Ru - C8	2.178 (3)
Ru - C4	2.173 (3)	Ru - C9	2.185 (3)
Ru - C5	2.182 (3)	Ru - C10	2.198 (3)
Ru - Cp*(cent)	1.806 (3)	Ru - Cp'(cent)	1.826 (3)
avg Cx - Cx'	1.499 (4)	C6 - C11	1.513 (4)
C11 - C14	1.543 (4)		
Bond Angles (°)			
Cent - Ru - Cent	176.1 (2)	C6 - C11 - C14	109.3 (2)
C6 - C11 - C13	110.2 (2)	C6 - C11 - C12	110.3 (3)
ring tilt	5.4 (3)	C1 - cent - cent - C6	2.0 (3)

Table 3-4. Selected Bond Lengths and Angles for $\text{Cp}^*\text{RuCpC}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{BPh}_3\text{Li}(\text{THF})_4(3-6)$.

Bond Distances (Å)			
Ru - C1	2.164 (3)	Ru - C6	2.185 (3)
Ru - C2	2.159 (3)	Ru - C7	2.182 (3)
Ru - C3	2.189 (3)	Ru - C8	2.186 (3)
Ru - C4	2.197 (3)	Ru - C9	2.201 (3)
Ru - C5	2.195 (3)	Ru - C10	2.220 (3)
Ru - Cp*(cent)	1.809 (3)	Ru - Cp'(cent)	1.830 (3)
avg Cx - Cx'	1.508 (5)	C10 - C13	1.525 (4)
C13 - C14	1.539 (4)	B - C32	1.641 (5)
B - C20	1.645 (4)	B - C26	1.648 (5)
B - C17	1.654 (4)		
Bond Angles (°)			
Cent - Ru - Cent	175.7 (2)	C10 - C13 - C11	110.1 (3)
C10 - C13 - C14	109.0 (2)	C10 - C13 - C12	109.6 (3)
ring tilt	6.4 (3)	C1 - cent - cent - C6	17.5 (3)
C17 - B - C26	104.5 (2)	C17 - B - C32	110.6 (2)
C17 - B - C20	112.5 (2)		

Table 3-5. ^1H and ^{13}C NMR Data

compound	assignt.	^1H NMR (in C_6D_6)	assignt.	^{13}C NMR (in C_6D_6)
LiCpC(CH ₃) ₂ PhBr ^a (3-1)	H4	5.73 (t, 2H)	C3	102.25
	H3	5.85 (t, 2H)	C4	102.72
	H9,H10	7.20 (s, 4H)	C5	129.82
	H7	1.67 (s, 6H)	C6	39.49
			C7	32.01
			C8	153.74
			C9	128.88
			C10	130.73
			C11	118.57
LiCpC(CH ₃) ₂ PhI ^a (3-2)	H4	5.63 (t, 2H)	C3	102.08
	H3	5.72 (t, 2H)	C4	102.47
	H9	7.10 (d, 2H)	C5	129.64
	H10	7.40 (d, 2H)	C6	39.60
	H7	1.67 (s, 6H)	C7	32.03
			C8	154.78
			C9	129.24
			C10	137.73
			C11	89.76
Cp*RuCpC(CH ₃) ₂ PhBr (3-3)	H4	4.00 (t, 2H)	C1	12.31
	H3	4.11 (t, 2H)	C2	84.96
	H9	7.01 (d, 2H)	C3	71.29
	H10	7.24 (d, 2H)	C4	73.17
	H1	1.88 (s, 15H)	C5	88.00
	H7	1.41 (s, 6H)	C6	37.96
			C7	29.94
			C8	151.30
			C9	127.84
			C10	131.12
			C11	126.22
Cp*RuCpC(CH ₃) ₂ PhI (3-4)	H4	4.00 (t, 2H)	C1	12.42
	H3	4.11 (t, 2H)	C2	84.99
	H9	7.01 (d, 2H)	C3	71.32
	H10	7.24 (d, 2H)	C4	73.20
	H1	1.88 (s, 15H)	C5	103.84
	H7	1.41 (s, 6H)	C6	38.05
			C7	29.89
			C8	151.48
			C9	128.74
			C10	137.23
			C11	91.04

Table 3-5(Cont'd) ^1H and ^{13}C NMR Data

compound	assignt.	^1H NMR	assignt	^{13}C NMR
$\text{Cp}^*\text{RuCpC}(\text{CH}_3)_2\text{PhBPh}_2\text{Py}$ (3-5)	H4	4.02 (t, 2H)	C1	11.95
	H5	4.30 (t, 2H)	C2	84.32
	(H9,H10,H13)	7.16 -	C3	71.24
	H14,H15)	7.52 (mult, 14H)	C4	72.52
	H17	6.10 (br t, 2H)	C5	105.41
	H18	6.54 (br t, 1H)	C6	37.57
	H16	8.24 (br d, 2H)	C7	29.85
	H1	1.90 (s, 15H)	C8	151.42
	H7	1.65 (s, 6H)	C9	127.33
			C10	134.63
			C11	not found
			C12	not found
			C13	134.77
			C14	127.43
			C15	127.56
			C16	123.56
			C17	124.94
			C18	125.17
$\text{Cp}^*\text{RuCpC}(\text{CH}_3)_2\text{PhBPh}_3\text{Li}^{\text{a}}$ (3-6)	H4	3.89 (t, 2H)	C1	12.39
	H5	4.17 (t, 2H)	C2	84.61
	H15	6.85 (t, 3H)	C3	71.79
	H14, H9	7.03 (t, 8H)	C4	72.41
	H10	7.44 (m, 2H)	C5	151.33
	H13	7.58 (m, 6H)	C6	38.20
	H1	1.83 (s, 15H)	C7	30.62
	H7	1.49 (s, 6H)	C8	135.80
			C9	136.33
			C10	123.40
			C11	not found
			C12	not found
			C13	121.64
			C14	137.04
			C15	125.60
$\text{Cp}^*\text{RuCpC}(\text{CH}_3)_2\text{PhBPh}_3$ $\text{Li}(\text{Et}_2\text{O})_1/2^{\text{ab}}$ (3-6a)	H4	4.01 (t, 2H)		
	H5	4.33 (t, 2H)		
	H15	7.08 (t, 3H)		
	H14, H9	7.10 (t, 8H)		
	H10	7.76 (m, 2H)		
	H13	7.86 (m, 6H)		
	H1	1.93 (s, 15H)		
	H7	1.66 (s, 6H)		
	Et_2O	1.10 (t, 3H)		
		3.25 (q, 2H)		

a. Drop of d^8 -THF added to increase solubility. b. No CNMR taken.

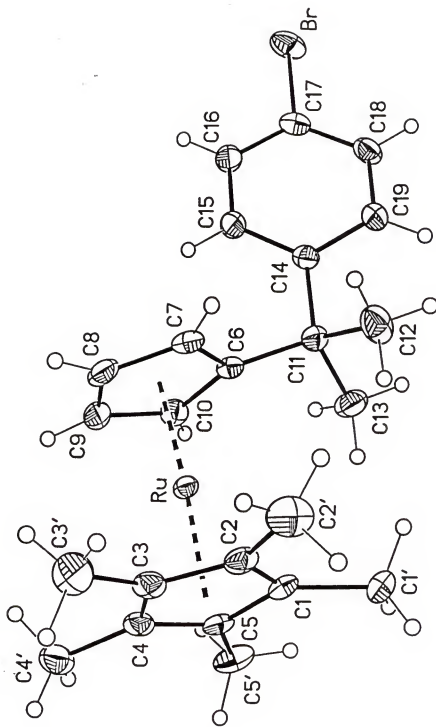


Figure 3-1. Thermal ellipsoid plot of 3-3, with ellipsoids drawn at the 50 % probability level.

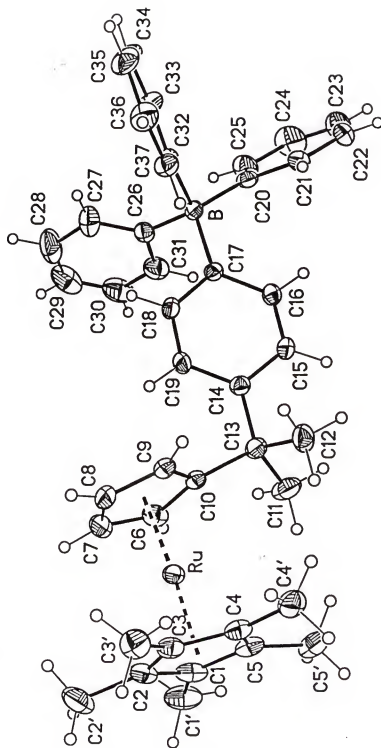


Figure 3-2. Thermal ellipsoid plot of 3-6b, with ellipsoids drawn at the 50 % probability level.

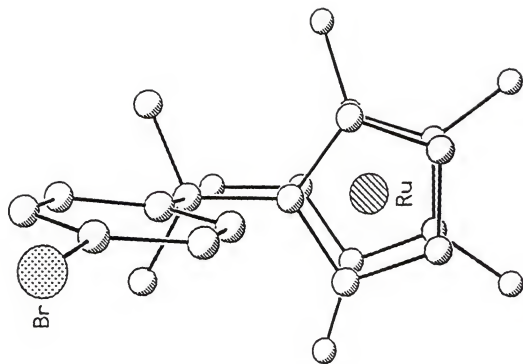


Figure 3-3. End-on view of 3-3, showing the eclipsed Cp rings and the molecular mirror-plane.

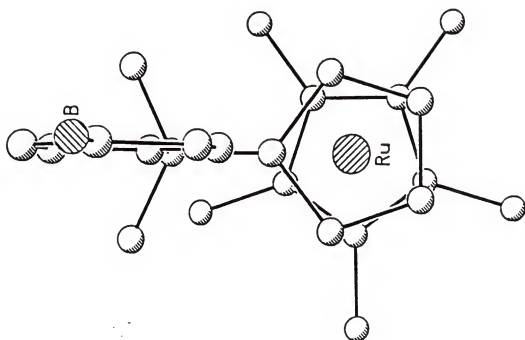


Figure 3-4. End-on view of **3-6b**, showing the slightly staggered Cp rings. The phenyl rings of the BPh₃ moiety have been omitted for clarity.

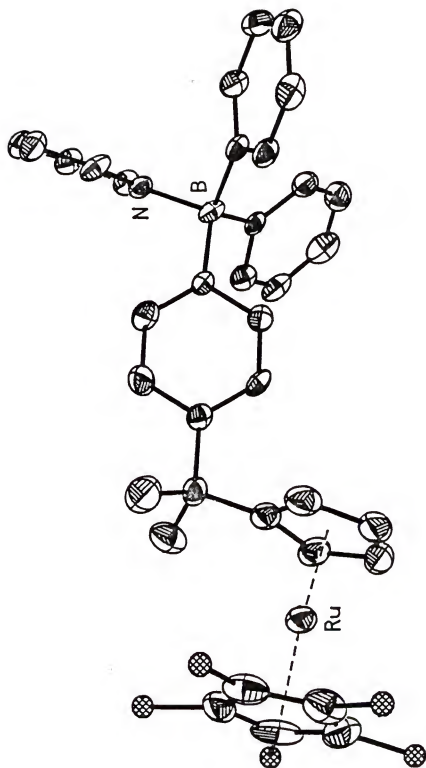


Figure 3-5. Plot showing the solid state structure of 3-5. An anisotropically refined structure could not be obtained

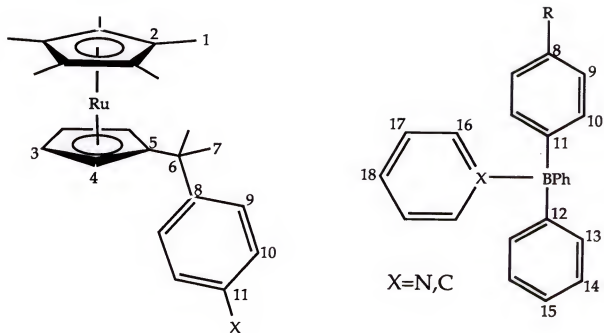


Figure 3-6. Numbering Scheme for NMR Data

X-Ray Structural Analyses

Single crystals of **3-3** were grown by cooling a hot, concentrated solution of **3-3** in hexanes. The structure has eclipsed Cp rings (Figures 1 and 3) and a molecular mirror-plane that passes through the plane of the phenyl ring and bisects each of the two Cp rings. The Cp rings are slightly tilted from parallel by 5.4° and the centroid-Ru-centroid angle is 176.1° . This diversion from the typical planarity occurs due to the interaction of the two methyl groups of C12 and C13 with the Cp* methyl group of C1' (Figure 1). The Ru-Cp* centroid distance is $1.806 \text{ \AA}$, which is comparable to the Ru-Cp* centroid distance of $1.803 \text{ \AA}$ in (pentaiodo)pentamethyl-ruthenocene^{70b} and $1.800 \text{ \AA}$ in decamethylruthenocene.^{70c} The Ru-CpC(CH₃)₂PhBr centroid distance is $1.826 \text{ \AA}$.

The crystal structure of **3-6b** was also solved after single crystals were grown by the slow diffusion of pentane into a concentrated THF solution of **3-6a**. The crystal structure of **3-6b** is similar to that of **3-3**, with one major exception being that the Cp rings are not eclipsed. In **3-6b**, the rings are twisted by 17.5° from the eclipsed position (Figures 2 and 4), which is approximately halfway between the eclipsed and staggered conformations. This staggering is apparently due to the packing of the molecules in the crystal because the bond lengths and angles of the ligands in the structures of both **3-3** and **3-6** are very similar (Tables 3 and 4). The two Cp rings are tilted from parallel by 6.4° and the centroid-Ru-centroid angle is 175.7° . The Ru-Cp* centroid distance is $1.809 \text{ \AA}$, and the Ru-CpC(CH₃)₂PhBPh₃ centroid distance is $1.830 \text{ \AA}$.

Examination of the crystal packing (not shown) of both structures reveals similar interactions between the C3' and C4' methyl groups of the Cp* and the *p*-substituted phenyl ring of an adjacent ruthenocene complex. In **3-**

6b, the Cp* ring has to rotate by 17.5° in order to accommodate such interactions, leading to the slightly staggered conformation. Other examples of non-eclipsed ruthenocenes^{70a, 70b, 78} have been observed, although the staggered conformation is rare.^{70c, 70d, 79} Only in cases where the Cp rings are extremely bulky, as in bis-tetraphenylruthenocene^{78b} and pentaiodo(pentamethyl)ruthenocene,^{70b} or when the ring rotation is locked by another covalently bound metal,^{78a} are the rings staggered. Decamethylruthenocene^{70c} and decachlororuthenocene^{79c} both maintain an eclipsed structure and the C-Cl bonds of decachlororuthenocene are lengthened and bent out of the plane of the Cp ring rather than staggering the conformation. Therefore, the half-staggered conformation of **3-6b** is somewhat unique and appears to be the first display of a staggered ruthenocene due to intermolecular packing conditions.

Oxidation Reactions with 3-6

The oxidation chemistry of many ruthenocenes has been examined,^{70c, 70d, 80} and a method to chemically oxidize Cp₂Ru(II) to Cp₂Ru(III) has not yet been found. When Cp₂Ru(II) is reacted with halogens,^{80a} the Cp₂Ru(II) complex is oxidized to the ruthenium(IV) halide cation. Attempts to stabilize Cp₂Ru(III) by altering the oxidants, oxidant ratios, solvents, and reaction conditions have not been successful.²⁶ However, by increasing the steric environment around the metal center by substituting Cp* for Cp, the decamethylruthenocenium(III) ion has been synthesized as a PF₆ salt.⁸¹ We have examined the ability of the tethered borate to stabilize the ruthenium(III) oxidation product and found that the borate does not stabilize the ruthenium(III) complex. Following the standard procedure^{80a} for oxidation of ruthenocene with iodine, oxidation reactions of **3-6a** with iodine

apparently leads to a ruthenium(IV) complex that has not been fully characterized.

The addition of three equivalents of I_2 to a solution of **3-6a** in carbon tetrachloride (CCl_4) leads instantly to the formation of a red precipitate which can be filtered and washed with CCl_4 . The product is diamagnetic and the ^1H NMR spectrum in CD_3CN suggests the presence of a ruthenium(IV) species. The two Cp resonances are shifted downfield and are more separated than in the original ruthenocene(II) complex. However, the aromatic region is obscure and does not integrate to the correct number of protons if simple oxidation of the metal occurred. Further studies on the oxidation of **3-6** are required to determine the nature of the observed chemistry.

Conclusions

p-Dihalobenzenes with 6,6-dimethylfulvene provides a useful starting point for the synthesis of derivitized Cp ligands, including borane- and borate-containing ligands. The substitution of the halogen is possible in the ruthenocene systems studied, and the synthesis of a novel borate-containing ruthenocene has been accomplished. This ruthenocene exhibits similar oxidation chemistry to other ruthenocenes, and the presence of the ligated borate does not stabilize the ruthenocenium(III) complex.

CHAPTER 4
SYNTHESIS, CHARACTERIZATION, AND STRUCTURE OF GROUP 4
METALLOCENES CONTAINING THE FUNCTIONALIZABLE
P-HALOPHENYL(DIMETHYL)METHYL-CYCLOPENTADIENYL LIGAND

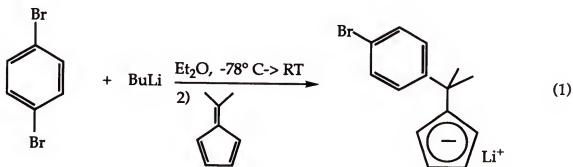
Introduction

Ion-pairing between a cationic metal active site and the associated counter-ion plays an important role in the reactivity of cationic transition metal polymerization catalysts.⁸² Typically, a very weakly-coordinating anion is preferred over a more strongly-coordinating anion in order to minimize the energy required to displace the anion with an incoming olefin. Many methods for minimizing the cation-anion interaction have been reported, including using bulky cyclopentadienyl (Cp) ligands to sterically hinder coordination of the anion,⁸³ using very bulky counter-anions,⁸⁴ and using fluorinated⁸⁵ and other charge-delocalized anion.⁸⁶ In 1985, Jordan and co-workers⁸⁷ first suggested that one method for decreasing the cation-anion interaction could be the synthesis of a zwitterionic catalyst system. Thus, if the cation-anion distance could be designed to maximize weak intra-molecular interactions and minimize inter-molecular ion-pairing, a tuneable, active catalyst system should be the result.

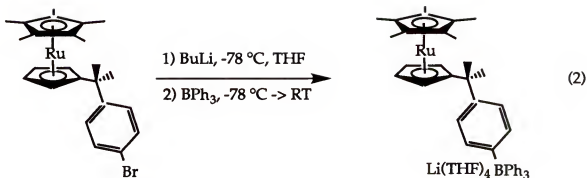
Many examples of zwitterionic systems have been reported⁸⁸ in which the inactive zwitterionic species must first dissociate into a cation-anion pair before becoming an active species. However, Bochmann and

coworkers⁸⁹ have recently reported a borate-containing zirconocene in which the borate is covalently bound directly to the Cp ring of the zirconocene. These systems are active polymerization catalysts, but seem to be inherently unstable and must still be activated with a Lewis acid cocatalyst. The observed instability is likely due to lability of the Cp-B bond. Recent work by Erker and coworkers⁹⁰ on more stable, covalently-bound borates seems more potentially useful; however, the borate is bound to the growing polymer chain, leading to increased charge separation and potential catalyst degradation during polymer isolation.

We have recently described the synthesis and reactivity of the functionalizable Cp ligand, $\text{LiCpC}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{Br}$, and demonstrated its usefulness for synthesizing borate- and borane-containing ruthenocenes.⁹¹ The ligand is prepared by the reaction of *p*-bromophenyllithium with 6,6-dimethylfulvene in ether (equation 1). The product of the reaction is a lithium salt of the Cp ligand, which can



react with a number of transition metal halides. We have shown that borate-containing ruthenocenes can be prepared by the reaction of $\text{Cp}^*\text{RuCpC}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{Br}$ with BuLi, and then trapping the resulting



lithiate with BPh_3 . After observing the ability of the ruthenocene complex to undergo the halo-lithium exchange reaction leading to a borate-containing ruthenocene, we examined the applicability of this new ligand to preparing zwitterionic group 4 Ziegler-type catalysts.

Experimental Section

General Considerations

All manipulations were performed under Ar by using standard Schlenk techniques or under N_2 in a Vacuum Atmospheres glove box. Glassware was oven dried prior to use. Solvents were distilled prior to use and stored over 4-Å molecular sieves in sealed bulbs under Ar. Diethyl ether and tetrahydrofuran were dried by distillation from Na/benzophenone ketyl. Pentane, toluene, and hexanes were dried by distillation from Na. NMR solvents were purchased from Cambridge Isotopes and were dried over 4-Å molecular sieves and not further purified. Cp^*ZrCl_3 ,⁹² $\text{LiCpC}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{Br}$,⁹¹ $\text{LiCpC}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{I}$,⁹¹ and $\text{B}(\text{C}_6\text{F}_5)_3$ ⁹³ were prepared according to literature methods. ZrCl_4 , BPh_3 , and BuLi (2.5M in hexanes) were purchased from Aldrich and used as

received. ^1H and ^{13}C NMR spectra were obtained by using either a Varian VXR-300, Gemini-300, or G.E. QE-300 spectrometer. Mass Spectra were obtained with a FinniganMAT MAT95Q Liquid Secondary Ion Mass Spectrometer (LSI MS, Cs^+); the selected $(m+1)/z$ values given refer to the isotopes ^1H , ^{12}C , ^{79}Br , ^{127}I , ^{35}Cl , and ^{91}Zr .

Procedures

$\text{Cp}^*(\text{CpC}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{Br})\text{ZrCl}_2$ (4-1a). To a mixture of Cp^*ZrCl_3 (0.50 g, 1.5 mmol) and $\text{LiCpC}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{Br}$ (0.40 g, 1.5 mmol) was added 30 mL toluene, and the mixture was refluxed for 80 hours. The solution became yellow, and the solid slowly became more flocculent. The solvent was removed *in vacuo*, and the resulting solid was dissolved in 25 mL CH_2Cl_2 and 25 mL of 3 M HCl. The CH_2Cl_2 layer was separated and dried over MgSO_4 , and the solvent was removed *in vacuo* yielding 4-1a (0.69 g, 82 %) as a white solid. ^1H NMR (C_6D_6) δ 1.74 (s, 15H, Cp^*), 1.83 (s, 6H, $\text{Cp-C}(\text{CH}_3)_2$), 5.46 (t, 2H, Cp-H_a), 6.08 (t, 2H, Cp-H_b), 6.75 (d, 2H, Ph-H_a), 7.20 (d, 2H, Ph-H_b). LSI MS: $(m+1)/z$ Calculated, 558. Found 558.

$\text{Cp}^*(\text{CpC}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{I})\text{ZrCl}_2$ (4-1b). To a mixture of Cp^*ZrCl_3 (0.50 g, 1.5 mmol) and $\text{LiCpC}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{I}$ (0.47 g, 1.5 mmol) was added 30 mL toluene, and the mixture was refluxed for 80 hours. The solution became yellow, and the solid slowly became more flocculent. The solvent was removed *in vacuo*, and the resulting solid was dissolved in 25 mL CH_2Cl_2 and 25 mL 3 M HCl. The CH_2Cl_2 layer was separated and dried over MgSO_4 , and the solvent was removed *in vacuo* yielding 4-1b (0.71 g, 78 %) as a yellow solid. ^1H NMR (C_6D_6) δ 1.74 (s, 15H, Cp^*), 1.82 (s, 6H, $\text{Cp-C}(\text{CH}_3)_2$), 5.46 (t, 2H, Cp-H_a), 6.08 (t, 2H, Cp-H_b), 6.63 (d, 2H, Ph-H_a), 7.40 (d, 2H, Ph-H_b). LSI MS: $(m+1)/z$ Calculated, 606. Found 606.

Cp*(CpC(CH₃)₂C₆H₄Br)ZrMe₂ (4-2a). To a solution of **4-1a** (0.50 g, 0.89 mmol) in 20 mL Et₂O at -78 °C was added MeMgBr (0.63 mL, 1.9 mmol) via syringe. The solution was warmed to room temperature over 30 min. and then stirred for an additional five hours. The mixture was filtered, the solvent removed *in vacuo*, and the resulting solid was washed with 15 mL hexanes. Drying *in vacuo* yielded **4-2a** (0.42 g, 90 %) as a white solid. ¹H NMR (C₆D₆) δ -0.27 (s, 6H, Zr-Me₂), 1.49 (s, 6H, Cp-C(CH₃)₂), 1.69 (s, 15H, Cp*), 5.46 (t, 2H, Cp-H_a), 5.70 (t, 2H, Cp-H_b), 6.84 (d, 2H, Ph-H_a), 7.24 (d, 2H, Ph-H_b). LSI MS: (m+1)/z Calculated, 518. Found 518.

Cp*(CpC(CH₃)₂C₆H₄I)ZrMe₂ (4-2b). To a solution of **4-1b** (0.50 g, 0.82 mmol) in 20 mL Et₂O at -78 °C was added MeMgBr (0.55 mL, 1.65 mmol) via syringe. The solution was warmed to room temperature over 30 min. and then stirred for an additional five hours. The mixture was filtered, the solvent removed *in vacuo*, and the resulting solid was washed with 15 mL hexanes. Drying *in vacuo* yielded **4-2b** (0.40 g, 87 %) as a yellow solid. ¹H NMR (C₆D₆) δ -0.27 (s, 6H, Zr-Me₂), 1.48 (s, 6H, Cp-C(CH₃)₂), 1.70 (s, 15H, Cp*), 5.46 (t, 2H, Cp-H_a), 5.70 (t, 2H, Cp-H_b), 6.72 (d, 2H, Ph-H_a), 7.45 (d, 2H, Ph-H_b). LSI MS: (m+1)/z Calculated, 566. Found 566.

(CpC(CH₃)₂C₆H₄Br)₂ZrCl₂ (4-3). To a mixture of ZrCl₄ (0.80 g, 3.4 mmol) and LiCpC(CH₃)₂C₆H₄Br (1.83 g, 6.8 mmol) was added 20 mL toluene and 5 mL THF. The colorless solution became yellow with the addition of THF, and the mixture was stirred for 10 hours at room temperature. The solvent was removed *in vacuo* and the resulting solid was dissolved in 25 mL CH₂Cl₂ and 25 mL 3M HCl. The CH₂Cl₂ layer was separated, dried over MgSO₄, and then the solvent removed *in vacuo* to yield **4-3** (1.52 g, 65 %) as an off-white solid. ¹H NMR (C₆D₆) δ 1.67 (s, 12H, Cp-C(CH₃)₂), 5.60 (t, 4H Cp-

H_a), 5.98 (t, 4H Cp-H_b), 6.72 (d, 4H Ph-H_a), 7.21 (d, 4H Ph-H_b). LSI MS: (m+1)/z Calculated, 684. Found 684.

(CpC(CH₃)₂C₆H₄Br)₂ZrMe₂ (**4-4**) To a solution of **4-3** (0.50 g, 0.73 mmol) in 20 mL Et₂O at -78 °C was added MeMgBr (1.6 mmol) via syringe. The solution was warmed to room temperature over 30 min. and then stirred for an additional five hours. The mixture was filtered, the solvent removed *in vacuo*, and the resulting solid was washed with 15 mL hexanes. Drying in *vacuo* yielded **4-4** (0.42 g, 89 %) as a white solid. ¹H NMR (C₆D₆) δ -0.008 (s, 6H, Zr-Me₂), 1.33 (s, 12H, Cp-C(CH₃)₂), 5.65 (t, 4H Cp-H_a), 5.67 (t, 4H Cp-H_b), 6.79 (d, 4H Ph-H_a), 7.24 (d, 4H Ph-H_b). LSI MS: (m+1)/z Calculated, 644. Found 644.

X-Ray Structural Analysis of 4-1a and 4-3. Data for both compounds were collected at 173 K on a Siemens CCD SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing MoK_α radiation (λ = 0.71073 Å). Cell parameters were refined using 6159 and 8192 reflections from data set 1 and 2 respectively. A hemisphere of data (1381 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1 %). Absorption corrections were applied based on the psi scan using the entire data sets

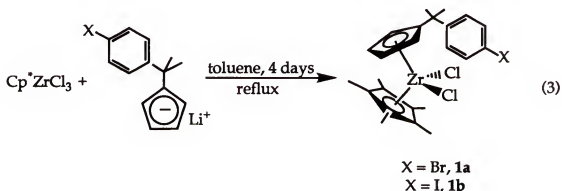
Both structures were solved by the Direct Methods⁹⁴ in SHELXTL and refined using full-matrix least squares on F². The non-H atoms were refined with anisotropic thermal parameters. All of the H atoms were located from Difference Fourier maps and refined without any constraints. For compound **4-1a**, 370 parameters were refined in the final cycle of refinement using 4481 reflections with I > 2σ(I) to yield R₁ and wR₂

of 2.96% and 7.33% respectively. And for compound 4-3, there were two independent complexes in the asymmetric unit and 820 parameters were refined in the final cycle of refinement using 7337 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 4.00% and 6.28%, respectively. Refinement was done using F^2 .

Results and Discussion

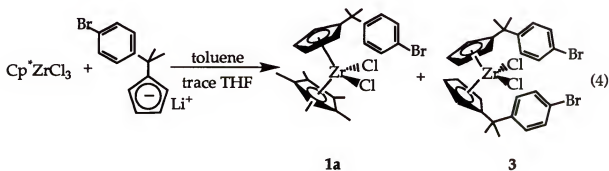
Syntheses

The zirconocene dichlorides were prepared according to standard procedures.⁹⁵ If a mixture of one equivalent of $\text{LiCp}^*(\text{CH}_3)_2\text{C}_6\text{H}_4\text{X}$ ($\text{X} = \text{Br}$, **1**) and one equivalent of Cp^*ZrCl_3 is refluxed in toluene for four days, the mixed-ligand zirconocene dichlorides, $\text{Cp}^*(\text{CpC}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{X})\text{ZrCl}_2$ ($\text{X} = \text{Br}$, **4-1a**; $\text{X} = \text{I}$, **4-1b**), are isolated after work-up in CH_2Cl_2 and aqueous HCl (equation 3). The addition of a small amount of ethereal solvents (Et_2O , THF) increased



the rate of the reaction considerably, probably due to increased solubility of both the lithium salt and the zirconium halide. However, the addition

of ethereal solvents invariably led to mixtures of the mixed-ligand zirconocene dichlorides, and the bis-substituted zirconocene dichlorides. For example, the addition of about one mL of THF to a mixture of Cp^*ZrCl_3 and $\text{LiCpC}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{Br}$ in 30 mL toluene leads to an immediate color change, and the reaction is complete after about five hours resulting in a 70 : 30 mixture of **4-1a** : **4-3** (equation 4). The mixture can be separated by extraction with hexanes due to the greater



solubility imparted by the Cp^* ligand; however, the necessity to separate the two products is avoided when the reaction is run in pure toluene.

The bis-substituted zirconocene dichloride, **4-3**, is also prepared by the reaction of two equivalents of $\text{LiCpC}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{Br}$ with one equivalent of ZrCl_4 in either refluxing toluene, or in a mixture of toluene and THF. The reaction with THF is preferred since the reaction is much faster, and there is no concern for the generation of mixed ligand products.

The syntheses of the dimethyl zirconocenes are all accomplished in the same manner. A solution of the zirconocene dichloride in Et_2O is



cooled to $-78\text{ }^{\circ}\text{C}$ and slightly more than two equivalents of MeMgBr is added. The reaction mixture is then warmed to room temperature and stirred overnight. The reaction product is then extracted with hexanes and the solvent removed to yield the solid dimethyl zirconocene. Other methylating agents were tried including MeLi, MeMgCl, and MeMgI, however with MeLi and MeMgCl, the product yields tended to be poor, and, with MeMgI, the product tended to contain more impurities.

Zirconocenes **4-1a** and **4-3** are active polymerization catalysts for ethylene when activated with MAO, however their activity was not noteworthy.

X-Ray Structural Analyses

The crystal structure of **4-1a** was determined after suitable, needle-shaped crystals were grown from cold hexanes. Selected bond lengths and angles are shown in Table 3. The coordination geometry is distorted tetrahedral around the metal center, with a Cl - Zr - Cl bond angle of 98.5° and a centroid - Zr - centroid angle of 130.8° . The Zr - Cp*(centroid)) distance is slightly shorter ($2.223\text{ \AA}$) than the other Zr - Cp'(centroid) ($2.233\text{ \AA}$) which is what is expected since the permethylated Cp ring is more electron rich, and can coordinate more tightly to the Lewis acidic metal center. The isopropyl

Table 4-1. Crystal data and structure refinement for 4-1a.

Empirical formula	C ₂₄ H ₂₉ Br Cl ₂ Zr
Formula weight	559.50
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 8.2630(2) Å, α = 82.6400(1)° b = 8.5654(2) Å, β = 86.8970(1)° c = 18.1709(4) Å, γ = 65.1230(1)°
Volume, Z	1157.12(5) Å ³ , 2
Density (calculated)	1.606 Mg/m ³
Absorption coefficient	2.441 mm ⁻¹
F(000)	564
Crystal size	0.30 x 0.15 x 0.10 mm
Theta range for data collection	2.26 to 27.50 deg.
Limiting indices	-11 ≤ h ≤ 6, -11 ≤ k ≤ 11, -23 ≤ l ≤ 24
Reflections collected	8014
Independent reflections	5172 [R(int) = 0.0237]
Absorption correction	Empirical
Min. & Max Transmission	0.525, 0.831
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5172 / 0 / 370
Goodness-of-fit on F ²	0.995
Final R indices [I > 2σ(I)]	R1 = 0.0296, wR2 = 0.0733 [4481]
R indices (all data)	R1 = 0.0361, wR2 = 0.0764
Extinction coefficient	0.0049(7)
Largest diff. peak and hole	0.577 and -0.592 e•Å ⁻³

Table 4-2. Crystal data and structure refinement for 4-3.

Empirical formula	C ₂₈ H ₂₈ Br ₂ Cl ₂ Zr
Formula weight	686.44
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 20.3610(2) Å, α = 90° b = 13.3953(2) Å, β = 110.468(1)° c = 20.8260(1) Å, γ = 90°
Volume, Z	5321.49(10) Å ³ , 8
Density (calculated)	1.714 Mg/m ³
Absorption coefficient	3.633 mm ⁻¹
F(000)	2720
Crystal size	0.32 × 0.11 × 0.04 mm
Theta range for data collection	1.73 to 27.50 deg.
Limiting indices	-20 ≤ h ≤ 27, -18 ≤ k ≤ 17, -26 ≤ l ≤ 23
Reflections collected	35688
Independent reflections	12056 [R(int) = 0.0689]
Absorption correction	Empirical
Min. & Max Transmission	0.624, 0.894
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	11979 / 0 / 820
Goodness-of-fit on F ²	0.935
Final R indices [I > 2σ(I)]	R1 = 0.0400, wR2 = 0.0628 [7337]
R indices (all data)	R1 = 0.0927, wR2 = 0.0777
Extinction coefficient	0.00047(4)
Largest diff. peak and hole	0.482 and -0.702 e•Å ⁻³

Table 4-3. Selected Bond Lengths and Angles for **4-1a**.

Bond Distances (Å)			
Zr-C1	2.629(2)	Zr-C21	2.513(2)
Zr-C2	2.566(2)	Zr-C22	2.529(2)
Zr-C3	2.464(2)	Zr-C23	2.539(2)
Zr-C4	2.468(2)	Zr-C24	2.531(2)
Zr-C5	2.547(2)	Zr-C25	2.545(2)
Zr-Cp'(cent.)	2.233(2)	Zr-Cp*(cent.)	2.223(2)
Zr-Cl1	2.4373(6)	Zr-Cl2	2.4585(6)
Bond Angles (deg)			
Cent-Zr-Cent	130.8(3)	Cl-Zr-Cl	98.5(3)
C1-C6-C9	107.6(3)		

Table 4-4. Selected Bond Lengths and Angles for **4-3a** and **4-3b**.

	Bond Distances (Å)	
	4-3a	4-3b
Zr-Cp'(cent.)	2.219(4)	2.219(4)
Zr-Cp'(cent.)	2.220(4)	2.224(4)
Zr-Cl1	2.4587(10)	2.446(10)
Zr-Cl2	2.4477(10)	2.449(10)
Zr-C1	2.580(4)	2.604(4)
Zr-C2	2.540(4)	2.560(4)
Zr-C3	2.510(4)	2.509(4)
Zr-C4	2.473(4)	2.450(4)
Zr-C5	2.515(4)	2.500(4)
Zr-C21	2.590(4)	2.602(4)
Zr-C22	2.515(4)	2.507(4)
Zr-C23	2.474(4)	2.460(4)
Zr-C24	2.498(4)	2.513(4)
Zr-C25	2.539(4)	2.551(4)
	Bond Angles (deg)	
	4-3a	4-3b
Cent-Zr-Cent	129.9(3)	129.4(3)
Cl-Zr-Cl	93.1(3)	93.5(3)
C1-C6-C9	107.5(3)	107.0(3)
C21-C26-C29	108.0(3)	107.5(3)

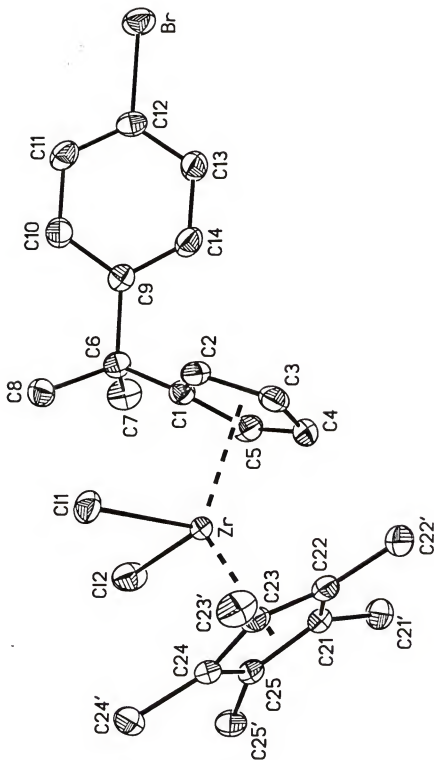


Figure 4-1. Thermal Ellipsoid Plot of 4-1a with thermal ellipsoids at the 50 % probability level. All hydrogen atoms are omitted for clarity.

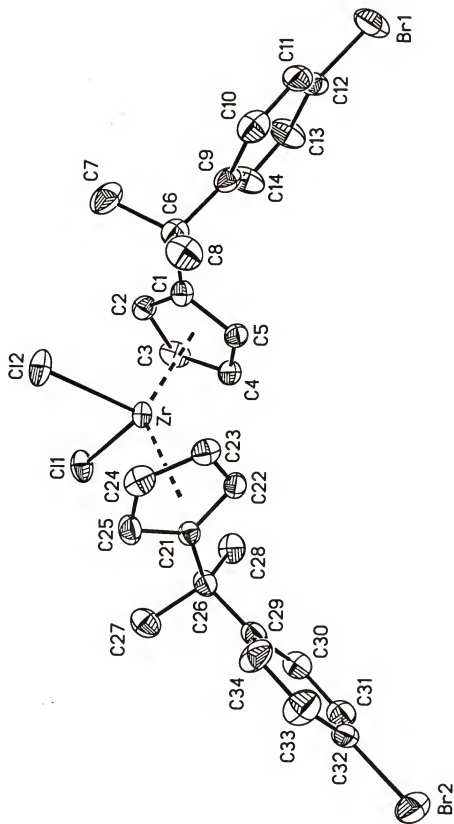


Figure 4-2. Thermal Ellipsoid Plot of 4-3a with thermal ellipsoids at the 50 % probability level. All hydrogen atoms are omitted for clarity.

bridge between the Cp ring and the phenyl ring is situated so that one of the methyl groups (C8) bisects the Cl - Zr - Cl angle, with the phenyl ligand pointed away from the metal center. This minimizes both steric and electronic repulsions between the electron rich phenyl ring and the Cl ligands.

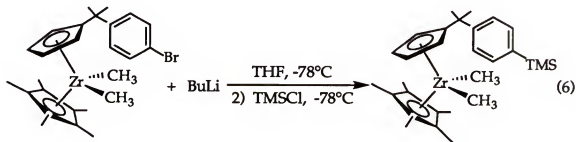
The crystal structure of **4-3** was determined after suitable, needle-shaped, crystals were grown from benzene/hexanes. The structure contained two chemically equivalent, but crystallographically independent complexes, which will be described here as **4-3a** and **4-3**.

Table 4-4 shows selected bond lengths and angles for **4-3a** and **4-3b**. In both **4-3a** and **4-3b**, the geometry around the metal center is distorted tetrahedral. In **4-3a**, the Cl - Zr - Cl bond angle is 93.1° and in **4-3b**, the angle is 93.5°. These angles are significantly more acute than in **4-1a**, and this can be attributed to the absence of the bulky methyl groups on the permethylated Cp ligand. In **4-3a**, the centroid - Zr - centroid angle is 129.9° and in **4-3b**, the angle is 129.4°. As expected, the two Zr - centroid distances in both **4-3a** and **4-3b** are the same, with distances of 2.219Å and 2.220Å in **4-3a**, and distances of 2.219Å and 2.224Å in **4-3b**. In both structures, the bulky groups on the Cp ligands are anti to each other and the phenyl groups are directed away from the metal center similar to that observed in the structure of **4-1a**.

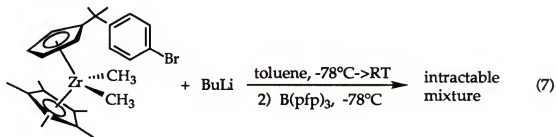
Reactions of Zirconocenes

Halo-lithium exchange reactions were attempted on the dimethyl complexes **4-2a** and **4-4** to avoid competition between halo-lithium exchange and alkylation of the metal center. Using standard conditions, one equivalent of BuLi was allowed to react with a solution of one

equivalent of dimethylzirconocene in THF at -78°C , followed by the addition of one equivalent of trimethylsilylchloride (TMSCl). After three hours of reaction time, the solution was evaporated and the product was



extracted in hexanes. The product, $\text{Cp}^*(\text{CpC}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{TMS})\text{ZrMe}_2$, was isolated in 30 % yield. This showed that the halo-lithium exchange reaction does work with the zirconocenes, so the analogous reaction was attempted with triarylboranes instead of TMSCl. Thus one equivalent of BuLi was allowed to react with a solution of one equivalent of dimethylzirconocene in THF at -78°C , followed by the addition of one equivalent of borane (BPh_3 or $\text{B}(\text{C}_6\text{F}_5)_3$). After about one hour at -78°C , the solution was slowly warmed to room temperature and stirred



overnight. The solvent was then removed *in vacuo*, and the reaction products invariably gave intractable mixtures of metal containing products. The desired product was observed by ^1H NMR *via* characteristic splitting patterns, however attempts to isolate the desired product failed. Other solvents including toluene, pentane, and Et_2O were used in attempts to yield cleaner reaction products, but intractable mixtures were still obtained.

Conclusions

The synthesis and reactivity of new zirconocenes based on the functionalizable Cp ligand, $\text{LiCpC}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{Br}$, have been examined, and these complexes are active olefin polymerization catalysts. However, unlike the similar ruthenocene systems with the same ligand, the zirconocene complexes do not cleanly undergo the halo-lithium exchange reaction. Other side reactions occur along with the halo-lithium exchange, probably owing to the more reactive, electron deficient metal center. Therefore, in order to prepare zwitterionic group 4 metal catalysts with a pendant borate group, the borate must first be affixed to the ligand before attaching the ligand to the metal center.

CHAPTER 5

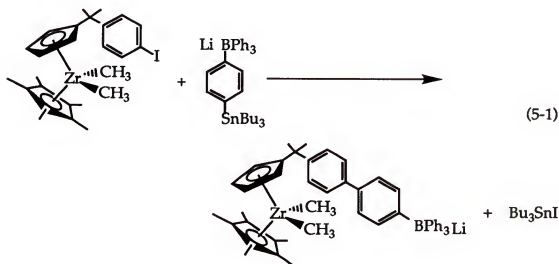
THE APPLICATION OF TIN COUPLING METHODS TO THE SYNTHESIS OF ZWITTERIONIC GROUP 4 METALLOCENES

Introduction

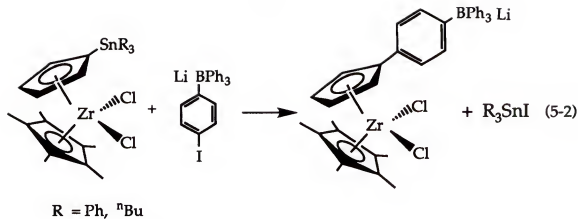
Nucleophilic attack at the exocyclic carbon of 6,6-dimethylfulvene occurs to form an anionic cyclopentadienyl (Cp) ligand, which can then be metathesized with a metal chloride, forming a new Cp-containing complex. In previous studies, we found that the reaction of *p*-bromophenyl lithium with dimethylfulvene leads to a functionalizable Cp ligand when bound to a ruthenium fragment. However, the same ligand is not functionalizable when bound to a zirconium fragment, because the more reactive zirconium metal center leads to side reactions. Therefore, we examined methods for the synthesis of a borate-containing Cp ligand prior to coordination to the metal center.

Our initial approach was to synthesize a functionalizable tetraarylborate, with which we could prepare a nucleophilic phenylborate that would react with 6,6-dimethylfulvene. In this way, the borate-containing ligand would be prepared prior to coordination to the metal, and the previously observed side reactions could be avoided. We approached the synthesis of a nucleophilic phenylborate using two methods; halo-lithium exchange, and tin coupling methods.

Trialkyl- and triaryl-tin reagents have been used as coupling reagents with aryl halides for preparing C-C bonds.⁹⁶ These reactions are driven by the formation of a strong Sn-X bond, where X is usually I. The coupling reactions can be catalyzed by late transition metal catalysts such as $\text{Pd}(\text{PPh}_3)_4$,⁹⁷ but also occur without the presence of catalysts.⁹⁶ There are two general methods possible for preparing borate-containing group 4 metallocenes by using tin coupling methods. One method (equation 5-1) involves the reaction of a tin- and borate-containing compound with a metallocene containing an aryl



iodide moiety. The other method (equation 5-2) involves the reaction of a tin-containing metallocene with a borate-containing aryl iodide. The application of both of these methods was examined, and the results will be discussed.



Experimental Section

General Considerations

All manipulations were performed under Ar by using standard Schlenk techniques or under N₂ in a Vacuum Atmospheres glove box. Glassware was oven dried prior to use. Solvents were distilled prior to use and stored over 4-Å molecular sieves in sealed bulbs under Ar. Diethyl ether and tetrahydrofuran were dried by distillation from Na/benzophenone ketyl. Pentane and hexanes were dried by distillation from Na. NMR solvents were purchased from Cambridge Isotopes and were dried over 4-Å molecular sieves and not further purified. Cp*ZrCl₃,⁴⁸ CpZrCl₃,⁹⁸ Cp(SnBu₃)₂,⁹⁹ and Cp(SnPh₃)₂⁹⁹ were prepared according to literature methods. *p*-Diodobenzene, *p*-dibromobenzene, 6,6-dimethylfulvene, and BuLi (2.5M in hexanes) were purchased from Aldrich and used as received.

¹H NMR spectra were obtained by using either a Varian VXR-300, Gemini-300, or G.E. QE-300. ¹¹B NMR spectra were obtained by using a Varian VXR-300 spectrophotometer. Mass Spectra were obtained with a FinniganMAT MAT95Q Liquid Secondary Ion Mass Spectrometer (LSI MS,

Cs⁺); the selected $m+1/z$ values given refer to the isotopes ¹H, ¹²C, ⁷⁹Br, ¹²⁷I, and ¹¹B.

Procedures

[*p*-BrC₆H₄BPh₃][Li(Et₂O)₄] (5-1a). To a solution of *p*-dibromobenzene (2.92 g, 12.0 mmol) in 50 mL Et₂O at -78 °C was added BuLi (4.96 mL, 12.0 mmol) and the solution warmed to room temperature over 30 min. This solution was added to a solution of BPh₃ (2.90 g, 12.0 mmol) in 30 mL Et₂O and white precipitate formed immediately. The mixture was stirred for two hours, filtered, and the white solid was washed with 20 mL hexanes. The solid was dried *in vacuo*, yielding **5-1a** (4.90 g, 98 %) as a white solid. ¹H NMR (C₆D₆, 23 °C): δ= 0.92 (t, 24H, OCH₂CH₃), 2.98 (q, 16H, OCH₂CH₃), 6.90 (t, 3H, *p*-Ph₃), 6.99 (t, 6H, *o*-Ph₃), 7.43 (d, 2H, *m*-Ph), 7.68 (br d, 2H, *o*-Ph), 7.83 (br d, 6H, *o*-Ph₃). LSI MS: m/z Calculated, 397. Found 397.

[*p*-IC₆H₄BPh₃][Li(Et₂O)₄] (5-1b). The same procedure was followed as described for **5-1a** yielding **5-1b** as a white solid (90 %). ¹H NMR (C₆D₆, 23 °C): δ= 0.58 (t, 24H, OCH₂CH₃), 2.69 (q, 16H, OCH₂CH₃), 6.91 (t, 3H, *p*-Ph₃), 7.11 (t, 6H, *o*-Ph₃), 7.55 (br d, 2H, *o*-Ph), 7.60 (d, 2H, *m*-Ph), 7.83 (br d, 6H, *o*-Ph₃). LSI MS: m/z Calculated, 446. Found 446.

[*p*-Bu₃SnC₆H₄BPh₃][Li(THF)₄] (5-2a). To a mixture of freshly cut Li (0.10 g, 14.4 mmol) in 30 mL THF at 0 °C was added Bu₃SnCl (0.67 mL, 2.47 mmol) and the mixture stirred for two hours. The mixture was then heated to reflux for 15 hours, and the solution became green. The green mixture was filtered and the filtrate was added directly to a solution of **5-1a** in 20 mL THF, and the mixture stirred for three days. The THF was removed *in vacuo* and the resultant solid was extracted twice with 30 mL benzene. The benzene was removed *in vacuo* yielding **5-2a** as a grey solid. ¹H NMR (C₆D₆, 23 °C): δ= 0.92

(t, 9H, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.20 (p, 16H, THF), 1.30 - 1.75 (m, 18H, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.08 (p, 16H, THF), 7.02 (t, 3H, *p*-Ph₃), 7.20 (t, 6H, *o*-Ph₃), 7.42 (d, 2H, *m*-Ph), 7.70 (br d, 2H, *o*-Ph), 7.87 (br d, 6H, *o*-Ph₃).

[*p*-Ph₃SnC₆H₄BPh₃][Li(THF)₄] (5-2b). To a mixture of freshly cut Li (0.10 g, 14.4 mmol) in 30 mL THF at 0 °C was added Ph₃SnCl (0.95 g, 2.46 mmol) and the mixture stirred for two hours. The mixture was then heated to reflux for four days, and the solution became brown. The mixture was filtered and the filtrate was added directly to a solution of **5-1b** in 20 mL THF, and the mixture stirred for three days. The THF was removed *in vacuo* and the resultant solid was extracted twice with 30 mL benzene. The benzene was removed *in vacuo* yielding **5-2b** as a white solid. ¹H NMR (C₆D₆, 23 °C): δ = 1.20 (p, 16H, THF), 3.05 (p, 16H, THF), 7.09 (m, 22H, Ph), 7.67 (m, 12H, Ph).

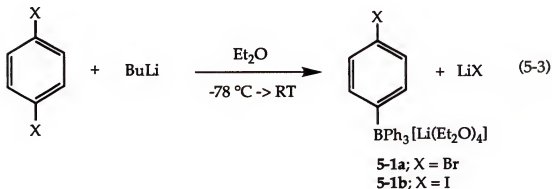
Cp*(CpSnBu₃)ZrCl₂ (5-3a). To a solution of Cp*ZrCl₃ (1.57 g, 4.72 mmol) in 50 mL toluene was added Cp(SnBu₃)₂ (2.29 mL, 4.72 mmol) and the mixture stirred at room temperature for one hour. The mixture was refluxed for an additional 15 hours and the solvent was removed *in vacuo*. The resultant oil was extracted twice with 20 mL pentane and dried *in vacuo* yielding a mixture of **5-3a** and Bu₃SnCl. Selected ¹H NMR data (C₆D₆, 23 °C): δ = 1.78 (s, 15H, Cp*), 5.82 (t, 2H, Cp-H_a), 6.48 (t, 2H, Cp-H_b).

Cp*(CpSnPh₃)ZrCl₂ (5-3b). The same procedure was followed as described for **5-3a** with the exception that **5-3b** was washed with hexanes and thus the product was able to be isolated from the Ph₃SnCl side product. Drying *in vacuo* yielded **5-3b** (40 %) as a yellow solid. ¹H NMR (C₆D₆, 23 °C): δ = 1.64 (s, 15H, Cp*), 5.98 (t, 2H, Cp-H_a), 6.52 (t, 2H, Cp-H_b), 7.0 - 7.3 (m, 9H, SnPh₃), 7.80 (d, 6H, SnPh₃).

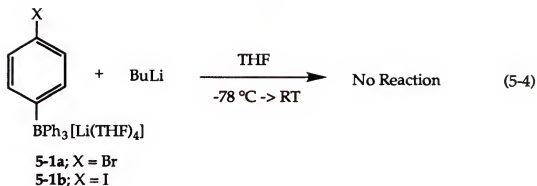
Results and Discussion

Syntheses

The syntheses of borates **5-1a** and **5-1b** are accomplished using the halo-lithium exchange reaction with the appropriate dihalobenzene in Et_2O , followed by addition of BPh_3 (equation 5-3). The new borates, which are insoluble in the relatively non-polar ether, precipitate as white solids and are easily isolated.



We first examined the possibility of using the halo-lithium exchange reaction again with these substituted borates in order to prepare a borate-containing phenyllithiate. Once the lithiate is formed, it should be able to react with 6,6-dimethylfulvene, yielding a dianionic, borate-containing Cp ligand which could then be attached to a group 4 metal. However, the halo-lithium exchange reaction does not occur when BuLi is added to a solution of borates **5-1a** or **5-1b** in THF at $-78\text{ }^\circ\text{C}$ (equation 5-4). Instead, no reaction is observed and the original borates are isolated. This lack of reactivity may be

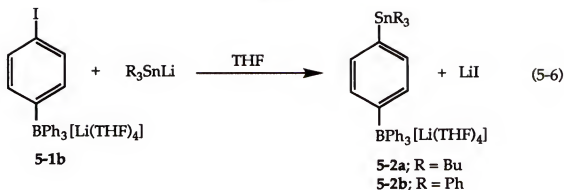


due to electron-donating effects of the triphenylboron group which destabilize the anionic lithiate. Therefore, we looked to other methods of preparing a carbanionic phenyl borate, and examined the possibility of forming trialkyl- and triaryltin reagents from our borates.

To prepare the tin-containing tetraphenylborates **5-2a** and **5-2b**, the LiSnR_3 is first prepared *in situ* by adding two equivalents of Li metal to a solution of the trialkyl-¹⁰⁰ or triaryltin¹⁰¹ chloride in THF (equation 5-5). Once the lithiate is formed, as indicated by a color change (green for Bu_3SnLi



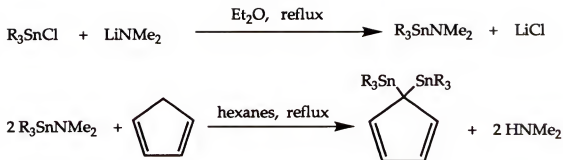
and brown for Ph_3SnLi), the mixture is filtered into a solution of **5-1b** in THF (equation 5-6). After three days, the reactions are complete, and removal of solvent under vacuum leads to the isolation of complexes **5-2a** and **5-2b**.



Since it has been determined that it is possible to prepare trialkyl- and triaryl tin complexes from the *p*-iodotetraphenylborate, more work should be done to examine if these complexes can be useful for preparing zwitterionic group 4 metallocenes. The most likely methods will be discussed in full in the future work section at the end of this chapter.

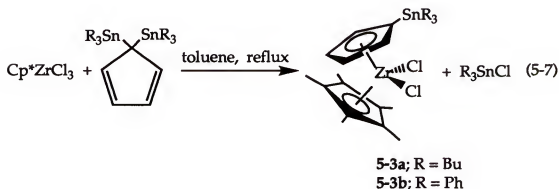
Another method for preparing zwitterionic group 4 metallocenes by using tin compounds involves the synthesis of tin-containing group 4 metallocenes, which can react with the *p*-iodotetraphenylborate **5-1b**, yielding a new C - C bond. This method was also examined, and new tin-containing group 4 metallocenes were developed and their reactivity was examined.

To prepare tin-containing metallocenes, bis-trialkyl- and bis-triarylCp compounds were prepared according to the procedure of Lappert and coworkers (Scheme 5-1). These compounds are prepared by the reaction of two equivalents of trialkyl- or triaryl tin dimethylamide with freshly cracked Cp in refluxing hexanes.



Scheme 5-1. Synthesis of bis-trialkyl- and triaryltin Cp compounds.

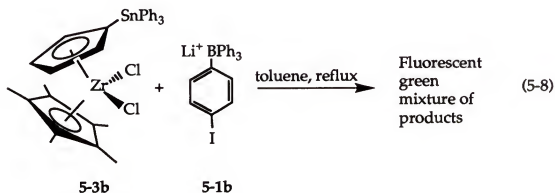
Once the bis-tin-Cp compounds are prepared, they are metathesized with Cp^*ZrCl_3 in refluxing toluene (equation 5-7) forming the new metallocene complexes $\text{Cp}^*(\text{CpSnBu}_3)\text{ZrCl}_2$, **5-3a**, and $\text{Cp}^*(\text{CpSnPh}_3)\text{ZrCl}_2$,



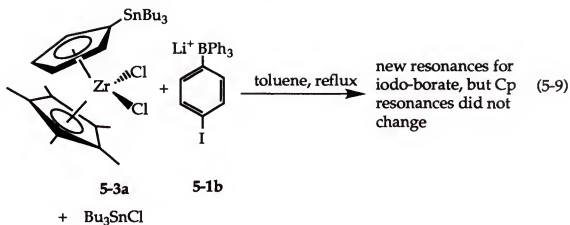
5-3b. The isolation of **5-3a** from the other product of the reaction, Bu_3SnCl , is difficult due to the high solubility imparted by both the permethylated Cp ligand and the long alkyl chains on the tin. Therefore, all further reactions with **5-3a** described herein contain one equivalent of Bu_3SnCl . The phenyl derivative **5-3b** has better solubility properties than **5-3a**, and can be isolated

from its side product, Ph_3SnCl , by simply washing the tin chloride out with hexanes.

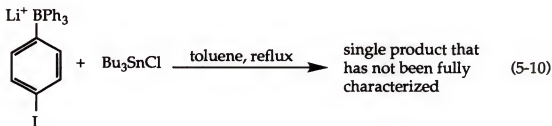
We chose **5-3b** for our initial study since it could be isolated as a pure complex. With this complex, we hoped to take advantage of the preference of vinylic- and allylic-tin bonds over aryl-tin bonds toward cleavage, assuming that a Cp ligand retained some vinylic or allylic character. Thus, if a mixture of **5-3b** and **5-1b** are refluxed in toluene overnight (equation 5-8), a fluorescent green color arises indicating a reaction has occurred. The resulting solution fluoresces when exposed to a UV lamp. However, examination of the product by ^1H NMR indicated that a reaction did occur, but the Cp resonances did not change. Thus, it seems likely that there is no preference for exchange of the Cp - Sn bond over the Ph - Sn bonds, and a biphenyl-borate is formed



instead. To avoid this problem, we examined the reaction of **5-3a** with **5-1b**, which should have a better specificity for Cp exchange as opposed to butyl exchange. However, with this reaction (equation 5-9) as well, the product displays no change in Cp resonances by ^1H NMR, although the borate resonances do change significantly.



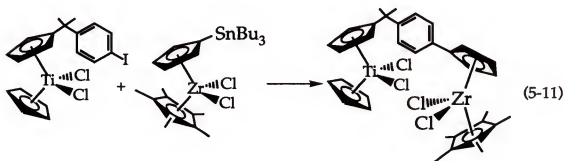
It was later found that **5-1b** reacts with one equivalent of Bu_3SnCl in refluxing toluene (equation 5-10) to give an undetermined product. Therefore, it seems likely that tin reagents can be used as coupling reagents, as shown by the coupling in the triphenyltin derivative. However more work needs to be done to determine the correct reaction conditions.



Future Work

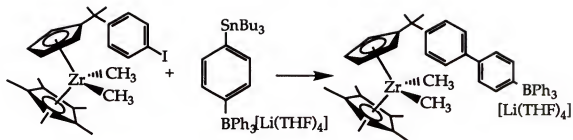
The chemistry of tin-containing organometallic compounds has not been actively explored in the chemical literature, and the results found in this preliminary study indicate that there is a wealth of opportunity to be found in

these compounds. The tin-containing metallocenes are especially interesting, and should be thoroughly studied. Considering the ability of tin reagents to couple and form C-C bonds, these Cp-tin metallocenes could lead into a great number of new, functionalized metallocene complexes. These compounds could be especially useful in the synthesis of bimetallic metallocenes. For



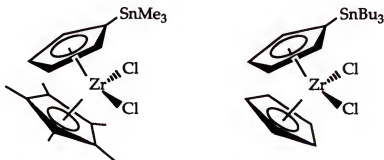
example, tin coupling reagents could be used in the synthesis of mixed metal bridged metallocenes (equation 5-11) which, due to the acidic nature of the protonated Cp and the complicated reactivity of Cp anions, can be especially difficult to synthesize.

More specific to the preliminary result discussed above, the application of tin coupling reagents to the synthesis of zwitterionic, borate-containing group 4 metallocenes should continue to be studied. The synthesis of tin-containing tetraphenylborates has been accomplished, and these reagents continue to be potential synthons for the preparation of borate-containing



metallocenes. The reactivity of these reagents with metallocenes containing aryl-iodide ligands should be explored.

Similarly, efforts to purify the tin-containing metallocenes that have been prepared in this study should be undertaken since preliminary results indicate that these reagents are useful coupling reagents. This should include the devising better purification methods for the known tributyltin-metallocene currently prepared, and the synthesis of new trialkyltin-Cp metallocene complexes that can be isolated from the tin-containing side products. Two likely methods for accomplishing this is the preparation of trimethyltin-Cp complexes and the use of CpZrCl₃. The suggested target molecules are indicated below.



It is expected that trimethyltin-Cp metallocenes will lack the high solubility imparted by the butyl groups in the tributyltin-complex. Similarly,

metallocenes containing the Cp* ligand are well known to be much more soluble than the non-methylated derivatives. Therefore, the use of Cp instead of Cp* should also lessen the solubility of the metallocene product, and the tin-chloride side product should be able to be washed away with hydrocarbon solvents such as pentane. In this manner, pure isolated samples of tin-containing metallocenes can be achieved, and since the transfer of phenyl and vinyl groups from tin are much more facile than the transfer of alkyl groups, these complexes should be useful synthons for preparing functionalized metallocenes.

CHAPTER 6

SYNTHESIS, CHARACTERIZATION, AND REACTIVITY OF NOVEL BORATE-CONTAINING BRIDGING CYCLOPENTADIENYL-SILYL-AMIDO COMPLEXES

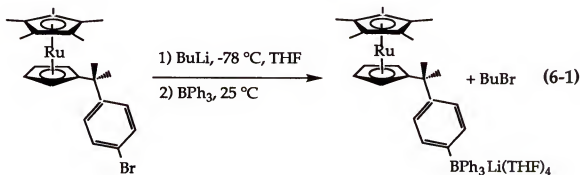
Introduction

The study of homogeneous, single-site α -olefin polymerization catalysts began as a method to determine the mechanism and active site of traditional heterogeneous Ziegler-type catalysts.⁷ However, after much progress in the understanding of homogeneous catalysis, it was quickly realized that there are many benefits of homogeneous catalysts over Ziegler-type systems. The ability to systematically alter the ligand environment and/or the co-catalyst in order to alter the polymer properties is perhaps the most important.¹⁴ Thus, a great deal of research has been devoted to the examination of effects of different ligands and co-catalyst systems.¹⁴

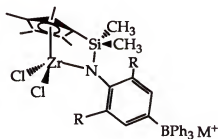
In the early 90's, Bercaw and co-workers^{11a, 11b} examined the effects on polymerization by changing the ligand environment of group 3 scandium systems from the bulky decamethylscandocene alkyl¹³ to the less hindered and more electrophilic $C_5Me_4Si(Me)_2NC(CH_3)_3ScR$ ("CpSiNRScR"). With this new ligand, they proposed that the active metal center would be more Lewis acidic and less sterically hindered than in the sandwich complex, improving olefin insertion. The results of their study indicate that these systems are highly active ethylene polymerization catalysts and, unlike the decamethylscandocene catalysts, will polymerize or oligomerize higher α -

olefins such as propylene, butene, and even pentene. Since then, this important new ligand system has been applied to group 4 catalyst systems, and many new ligands with various cyclopentadienyl (Cp) derivatives and different amine groups, have been developed.¹⁰² Furthermore, catalysts containing these ligands have finally helped move homogeneous catalysts out of the academic setting and into industrial applications. These catalysts have a relatively unhindered active site which leads to high activity and allows for the co-polymerization of higher α -olefins with ethylene.

We have been interested in the synthesis of zwitterionic, borate-containing homogeneous catalyst systems, in which the borate group is covalently bound through some linker, to the Cp ligand. A catalyst of this type might give some control of ion-pairing with the active metal cation and, once prepared as a zwitterion, would not need the addition of a co-catalyst for each polymerization reaction. We have recently reported the use of the halo-lithium exchange reaction in the preparation of borate-containing metallocenes, and have showed its potential in the synthesis of borate-containing ruthenocene complexes. This is accomplished by the reaction



(equation 6-1) of a bromo-phenyl-substituted metallocene with butyllithium (BuLi) followed by the addition of triphenylboron (BPh₃). This reaction works well for the unreactive 18 electron ruthenocene systems, however when we applied this reaction to electron-deficient zirconocene systems, mixtures of products were achieved that could not be separated. This is due to the higher reactivity of the Lewis acidic zirconium center, so we began to examine other methods for preparing borate-containing ligands prior to coordination to the metal center. This was accomplished by the synthesis of borate-containing "CpSiNR" ligands like that depicted below. The methods for their preparation are discussed herein.



Experimental Section

General Considerations

All manipulations were performed under Ar by using standard Schlenk techniques or under N₂ in a Vacuum Atmospheres glove box. Glassware was oven dried prior to use. Solvents were distilled prior to use and stored over 4-Å molecular sieves in sealed bulbs under Ar. Diethyl ether and tetrahydrofuran were dried by distillation from Na/benzophenone ketyl. Pentane was dried by distillation from Na. Methanol was purchased from Fisher and used as received. NMR solvents were purchased from Cambridge

Isotopes and were dried over 4-Å molecular sieves and not further purified. TMSCl was purchased from Aldrich and distilled prior to use. *p*-bromo-2,6-diisopropylaniline,¹⁰³ Me₄CpHSiMe₂Cl,^{11b} and Zr(NMe₂)₄¹⁰⁴ were prepared according to literature methods. *p*-bromoaniline, *p*-bromo-2,6-dimethylaniline, BPh₃, Bu₄NF·H₂O, ZrCl₄, LDA (2.0M in heptane/ethylbenzene/THF), and BuLi (2.5M in hexanes) were purchased from Aldrich and used as received.

¹H and ¹³C NMR spectra were obtained by using either a Varian VXR-300, Gemini-300, or G.E. QE-300 spectrophotometer. ¹¹B NMR spectra were obtained on a Varian VXR-300 spectrophotometer. Mass Spectra were obtained with a FinniganMAT MAT95Q Liquid Secondary Ion Mass Spectrometer (LSI MS, Cs⁺); the selected (*m*+1)/*z* values given refer to the isotopes ¹H, ¹²C, ⁷⁹Br, ¹²⁷I, ¹¹B, ¹⁵N, ⁹¹Zr, ³⁵Cl, and ²⁸Si.

Procedures

***p*-BrC₆H₄NHSiMe₂CpHMe₄ (6-1a).** To a solution of *p*-bromoaniline (1.00 g, 5.81 mmol) in 25 mL Et₂O at -78° C was added BuLi (2.33 mL, 5.81 mmol) and the solution stirred for 30 min, during which time, a yellow precipitate formed. To this mixture was added a cooled solution of Me₄CpHSiMe₂Cl (1.25 g, 5.81 mmol) in 15 mL Et₂O, and the mixture was stirred for four hours, filtered, and the Et₂O removed *in vacuo* yielding **6-1a** (1.70 g, 91%) as a yellow viscous oil. ¹HNMR spectrum (25 °C, C₆D₆): δ = 7.19 (d, 2H), 6.23 (d, 2H), 2.92 (br s, 2H), 1.85 (s, 6H), 1.78 (s, 6H), 0.00 (s, 6H).

(*p*-BrC₆H₄NSiMe₂CpMe₄)Zr(NMe₂)₂ (6-1b). To a solution of **6-1a** (0.80 g, 2.3 mmol) in 20 mL Et₂O was added Zr(NMe₂)₄ (0.70 g, 2.6 mmol) and the solution stirred for six hours. The Et₂O was removed *in vacuo*, and the resulting solid extracted twice with 20 mL hexanes. Concentrating the

hexanes *in vacuo* followed by cooling to -40°C led to large, colorless, single crystals of **6-1b** (0.94 g, 78%). ^1H NMR spectrum (25°C , C_6D_6): $\delta = 7.30$ (d, 2H), 6.73 (d, 2H), 2.75 (s, 12H), 2.10 (s, 6H), 1.84 (s, 6H), 0.59 (s, 6H). ^{13}C NMR spectrum (25°C , C_6D_6): $\delta = 152.2, 132.2, 132.1, 125.0, 123.0, 111.4, 100.9, 43.0, 42.9, 13.9, 10.9, 4.0$.

***p*-BrC₆H₄N(TMS)SiMe₂CpHMe₄ (6-1c).** To a solution of **6-1a** (1.10 g, 3.14 mmol) in 25 mL Et₂O at -78°C was added LDA (1.30 mL, 3.14 mmol) *via* syringe, and the solution stirred at -78°C for 30 min. To this solution was added TMSCl (0.45 mL, 3.53 mmol) and the solution was stirred at -78°C for 30 min before slowly warming to room temperature. The mixture was then filtered and the Et₂O removed *in vacuo* yielding **6-1c** (0.96 g, 72%) as a yellow viscous oil. ^1H NMR spectrum (25°C , C_6D_6): $\delta = 7.18$ (d, 2H), 6.65 (d, 2H), 2.80 (s, 1H), 1.95 (s, 6H), 1.75 (s, 6H), 0.06 (s, 9H), 0.02 (s, 6H). ^{13}C NMR spectrum (25°C , C_6D_6): $\delta = 147.0, 136.3, 132.9, 132.0, 131.7, 118.4, 17.36, 55.8, 15.0, 11.4, 2.3, 1.4$.

Li(THF)₄ [*p*-BPh₃C₆H₄N(TMS)SiMe₂CpHMe₄](6-1d). To a solution of **6-1c** (0.50 g, 1.18 mmol) in 30 mL THF at -78°C , was added BuLi (0.47 mL, 1.18 mmol) and the solution was stirred for 30 min. This solution was then added to a mixture of BPh₃ in THF at -78°C , and the mixture stirred 30 min before being warmed to room temperature. All BPh₃ dissolved during this time, and the solution was stirred at room temperature for an additional eight hours. The solution was concentrated *in vacuo* to five mL, and 30 mL pentane was added. An oil formed and the supernatant solution was decanted away. The oil was washed twice with 20 mL pentane and was dried *in vacuo* yielding **6-1d** (0.85 g, 82%) as a viscous oil. ^1H NMR spectrum (25°C , C_6D_6): $\delta = 7.46$ (m, 6H), 7.34 (m, 2H), 6.95 (t, 6H), 6.84 (t, 3H), 6.76 (d, 2H), 3.50 (m, 16H), 2.95 (br s, 1H), 1.92 (s, 6H), 1.65 (s, 6H), 1.54 (m, 16H), 0.02 (s, 9H), -0.12 (s, 6H).

Li(THF)₄ [*p*-BPh₃C₆H₄N(TMS)SiMe₂CpLiMe₄] (6-1e). To a solution of **6-1d** (0.60 g, 0.68 mmol) in 30 mL THF at -78 °C was added BuLi (0.27 mL, 0.68 mmol) and the yellow solution immediately became darker. The solution warmed to room temperature and stirred for eight hours. The red solution was concentrated to five mL *in vacuo* and 30 mL pentane was added. A yellow oil formed, and the supernatant solution was decanted away. The oil was washed twice with 20 mL pentane and solidified into a finely divided solid. The solid was filtered and dried *in vacuo* yielding **6-1e** (0.50 g, 81 %) as a yellow solid. ¹HNMR spectrum (25 °C, C₆D₆/d⁸-THF): δ = 7.55 (m, 6H), 7.42 (m, 2H), 7.00 (t, 6H), 6.87 (t, 3H), 6.76 (d, 2H), 3.51 (m, 16H), 1.98 (s, 6H), 1.70 (s, 6H), 1.53 (m, 16H), 0.06 (s, 9H), -0.06 (s, 6H). ¹³CNMR spectrum (25 °C, C₆D₆/d⁸-THF): δ = 140.3, 137.1, 135.1, 133.8, 127.4, 125.6, 121.6, 67.3, 25.0, 15.0, 11.2, 2.6, 0.4.

Li(THF)₄ [(*p*-BPh₃C₆H₄N(TMS)SiMe₂CpMe₄)ZrCl₃] (6-1f). To a solution of **6-1e** (0.10 g, 0.11 mmol) in 10 mL THF at -78°C was added a solution of ZrCl₄ (0.03 g, 0.12 mmol) in 10 mL THF, and the solution was warmed to room temperature. The solution was stirred for three hours and then the solvent was concentrated *in vacuo* to approximately five mL. To this was added 20 mL pentane and a yellow oil precipitated. The supernatant solution was decanted away and the oil was dried *in vacuo* yielding **6-1f** (0.12 g, 83 %) as a yellow solid. ¹HNMR spectrum (25 °C, C₆D₆/d⁸-THF): δ = 7.52 (m, 6H), 7.40 (m, 2H), 6.98 (t, 6H), 6.84 (t, 3H), 6.75 (d, 2H), 3.51 (m, 16H), 1.96 (s, 6H), 1.70 (s, 6H), 1.53 (m, 16H), 0.06 (s, 9H), -0.06 (s, 6H). ¹¹BNMR spectrum (25 °C, C₆D₆/CD₃CN): δ = -6.45.

2,6-Me₂C₆H₃NHSiMe₂CpHMe₄ (6-2a) To a solution of 2,6-dimethylaniline (0.29 mL, 2.3 mmol) in 25 mL Et₂O at -78° C was added BuLi (0.93 mL, 2.3 mmol) and a yellow solid formed. The mixture was warmed to

room temperature over 20 min, during which time, the solid redissolved. To this mixture was added a solution of $\text{Me}_4\text{CpHSiMe}_2\text{Cl}$ (0.50 g, 2.3 mmol) in 10 mL Et_2O , and the mixture was stirred for eight hours, filtered, and the Et_2O removed *in vacuo* yielding **6-2a** (0.75 g, 93%) as a colorless, viscous oil.

^1H NMR spectrum (25 °C, C_6D_6): δ = 6.96 (d, 2H), 6.82 (t, 1H), 2.82 (br s, 1H), 2.38 (br s, 1H), 2.10 (s, 6H), 1.95 (s, 6H), 1.80 (s, 6H), 0.10 (s, 6H). ^{13}C NMR spectrum (25 °C, C_6D_6): δ = 143.1, 136.0, 130.6, 128.3, 121.3, 121.2, 121.1, 19.3, 14.1, 10.8, -0.6.

(2,6-Me₂C₆H₃NSiMe₂CpMe₄)Zr(NMe₂)₂ (6-2b). To a solution of **6-2a** (0.70 g, 2.3 mmol) in 10 mL C_6H_6 was added $\text{Zr}(\text{NMe}_2)_4$ (0.65 g, 2.3 mmol) and the solution stirred for six hours. The C_6H_6 was removed *in vacuo*, and the resulting solid was washed with 20 mL hexanes. Concentrating the hexanes followed by cooling to -40° C led to a second crop of **6-2b** as large, colorless, crystals. Overall yield (0.84 g, 76%).

^1H NMR spectrum (25 °C, C_6D_6): δ = 7.14 (d, 2H), 6.89 (t, 1H), 2.71 (s, 12H), 2.31 (s, 6H), 2.30 (s, 6H), 1.90 (s, 6H), 0.50 (s, 6H). ^{13}C NMR spectrum (25 °C, C_6D_6): δ = 149.4, 133.0, 128.6, 125.5, 121.5, 43.0, 19.9, 14.3, 11.1, 5.6.

[2,6-Me₂C₆H₃NSiMe₂CpMe₄] Li₂ (6-2c). To a solution of **6-2a** (0.69 g, 2.3 mmol) in 20 mL THF at -78°C was added BuLi (0.93 mL, 2.3 mmol) and the solution was warmed to room temperature over 30 min. The solution stirred an additional five hours before being concentrated *in vacuo* to a volume of approximately five mL. To this was added 30 mL pentane, and a yellow precipitate formed. The solid was filtered, washed with 20 mL pentane, and then dried *in vacuo* yielding **6-2c** (0.69 g, 96%) as a white solid. ^1H NMR spectrum (25 °C, $\text{C}_6\text{D}_6/\text{d}^8\text{-THF}$): δ = 6.80 (d, 2H), 6.57 (t, 1H), 2.20 (s, 6H), 2.19 (s, 6H), 2.00 (s, 6H), 0.43 (s, 6H).

(2,6-Me₂C₆H₃NSiMe₂CpMe₄)ZrCl₂ (6-2d). To a solution of ZrCl_4 (0.13 g, 0.54 mmol) in 30 mL THF at -78°C was added a solution of **6-2c** (0.20 g, 0.54

mmol) in 10 mL THF and the solution was warmed to room temperature.

The solution stirred at room temperature for two hours and then the solvent was removed *in vacuo*. The solid was washed with 30 mL pentane and dried *in vacuo* yielding **6-2d** (0.26g, 65%) as a yellow solid. ^1H NMR spectrum (25 °C, $\text{C}_6\text{D}_6/\text{d}^8\text{-THF}$): δ = 6.86 (d, 2H), 6.65 (t, 1H), 2.04 (s, 6H), 1.84 (s, 6H), 1.72 (s, 6H), 0.43 (s, 6H).

***p*-Br-2,6-Me₂C₆H₂NHSiMe₂CpHMe₄ (6-3).** To a solution of *p*-bromo-2,6-dimethylaniline (0.30 g, 1.5 mmol) in 25 mL THF at -78° C was added LDA (0.75 mL, 1.5 mmol) and the solution stirred for 30 min, during which time, a yellow precipitate formed. To this mixture was added a cooled solution of Me₄CpHSiMe₂Cl (0.32 g, 1.5 mmol) in 15 mL THF, and the mixture was stirred for four hours, filtered, and the THF removed *in vacuo* yielding **6-3** as a yellow viscous oil. ^1H NMR spectrum (25 °C, C_6D_6): δ = 7.10 (s, 2H), 2.81 (br s, 1H), 2.20 (br s, 1H), 1.90 (s, 6H), 1.89 (s, 6H), 1.75 (s, 6H), 0.05 (s, 6H).

***p*-BrC₆H₄N(TMS)Li(Et₂O)_{1/2} (6-4a).** To a solution of *p*-bromoaniline (5.02 g, 29.2 mmol) in 60 mL Et₂O at -78 °C was added BuLi (12.0 mL, 29.2 mmol) and the mixture was warmed to RT over 20 min during which time, a yellow precipitate formed. To this mixture was added TMSCl (4.0 mL, 29.2 mmol) *via* syringe, and all solid dissolved. After stirring for 30 min, the solution was cooled to -78° C and BuLi (12.0 mL, 29.2 mmol) was added. The mixture stirred at -78 °C for one hour before slowly warming to RT. The mixture was stirred for two hours at 25 °C and then was filtered and the solvent removed *in vacuo* yielding **6-4a** (9.0 g, 96%) as a white solid. ^1H NMR spectrum (25 °C, C_6D_6): δ = 7.28 (d, 2H), 6.58 (br d, 2H), 2.48 (q, 2H), 0.70 (t, 3H), 0.28 (s, 9H).

***p*-BrC₆H₄N(TMS)₂ (6-4b).** To a solution of *p*-bromoaniline (5.02 g, 29.2 mmol) in 60 mL THF at -78 °C was added LDA (12.0 mL, 29.2 mmol) and the

mixture was stirred for 15 min. To this solution was added TMSCl (4.0 mL, 29.2 mmol), and the solution was stirred for 15 min. A second equivalent of LDA (12.0 mL, 29.2 mmol) was added, and the mixture stirred for 15 min before adding another equivalent of TMSCl (4.0 mL, 29.2 mmol). The solution was warmed to room temperature and stirred for one hour. The solvent was removed *in vacuo*, and the residue was extracted twice with 30 mL pentane. The pentane was removed *in vacuo* yielding **6-4b** (8.9 g, 97%) as an orange liquid. ^1H NMR spectrum (25 °C, C_6D_6): δ = 7.18 (d, 2H), 6.52 (d, 2H), 0.02 (s, 18H). ^{13}C NMR spectrum (25 °C, C_6D_6): δ = 147.5, 132.2, 132.2, 117.8, 2.0.

Alternate route to 6-4b. To a solution of **6-4a** (9.0 g, 28.0 mmol) in 60 mL THF at -78 °C was added TMSCl (4.0 mL, 29.2 mmol) and the solution was warmed to 25 °C over 30 min. The solution was stirred at 25 °C for eight hours and then the solvent was removed *in vacuo*. The resulting oily solid was extracted with 3 x 25 mL pentane. The pentane was removed *in vacuo* yielding **6-4b** (8.25 g, 94%) as an orange liquid.

[*p*-BPh₃C₆H₄N(TMS)₂][Li(THF)₄] (6-4c). To a solution of **6-4b** (4.44 g, 14.0 mmol) in 50 mL THF at -78 °C was added BuLi (5.6 mL, 14.0 mmol) and the solution was stirred for 30 min. This solution was added to a mixture of BPh₃ (3.40 g, 14.0 mmol) in 20 mL THF at -78 °C and the mixture stirred for two hours during which all solid dissolved. The mixture was then warmed to 25 °C and stirred for eight hours. The solvent was removed *in vacuo* and the resulting solid washed with 3 x 20 mL pentane and then dried *in vacuo* yielding **6-4c** (9.89 g, 91%) as a white solid. ^1H NMR spectrum (25 °C, $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): δ = 7.48 (br m, 6H), 7.31 (br m, 2H), 7.00 (t, 6H), 6.83 (t, 3H), 6.64 (d, 2H) 3.48 (m, 16H), 1.52 (m, 16H), 0.00 (s, 18H). ^{13}C NMR spectrum (25 °C, $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): δ = 136.5, 135.4, 126.0, 125.85, 125.8, 125.7, 122.0, 121.6, 67.8, 25.6, 2.2.

[*p*-BPh₃C₆H₄N(TMS)₂] PPN (6-4d). To a solution of 6-4c (1.0 g, 1.4 mmol) in acetonitrile was added PPNCl (0.82 g, 1.4 mmol) and a white solid immediately precipitated. The mixture was stirred for eight hours and the acetonitrile was removed *in vacuo* yielding an oily solid. The solid was dissolved in 10 mL THF and 40 mL pentane was slowly added, precipitating a white solid. The solid was filtered and then washed with 30 mL pentane and dried *in vacuo* yielding 6-4d (1.1 g, 96%) as a white solid. ¹HNMR spectrum (25 °C, C₆D₆/CD₃CN): δ = 7.40 - 7.10 (m, 36H), 7.00 (br m, 2H), 6.90 (t, 6H), 6.75 (t, 3H), 3.48 (m, 16H), 1.99 (s, 6H), 1.50 (m, 16H), -0.05 (s, 18H).

[*p*-BPh₃-C₆H₄NH₂][Li(THF)₄] (6-4e). 6-4c (5.6 g, 8.7 mmol) was dissolved in 15 mL MeOH (not dried) and the solution was stirred for two to four days. The solvent was then removed *in vacuo* and the resulting solid was dissolved in 20 mL THF and stirred for eight hours. The solvent was then concentrated *in vacuo* to five mL and 20 mL pentane added causing a colorless precipitate to form, which was isolated by filtration. The solid was dried *in vacuo* yielding 6-4e (3.85 g, 91%) as an off-white solid. ¹HNMR spectrum (25 °C, C₆D₆/CD₃CN): δ = 7.64 (m, 6H), 7.40 (m, 2H), 7.08 (t, 6H), 6.88 (t, 3H), 6.50 (d, 2H), 3.49 (m, 16H), 3.20 (br s, 2H), 1.50 (m, 16H). ¹³CNMR spectrum (25 °C, C₆D₆/CD₃CN): δ = 136.9, 136.5, 126.4, 125.9, 121.9, 114.9, 67.7, 25.6. ¹¹BNMR spectrum (25 °C, C₆D₆/CD₃CN): δ = -6.45.

[*p*-BPh₃-C₆H₄NH₂] PPN (6-4e). To a mixture of 6-4d (1.0 g, 1.1 mmol) in 15 mL THF was added 15 mL THF and all solid dissolved. The solution was heated to reflux for 12 hours, and then cooled to room temperature and the THF was removed *in vacuo*. When all THF was removed, a tan solid precipitated, which was filtered and washed with 20 mL benzene. The solid was dried *in vacuo* yielding 6-4e (0.76, 86%) as a tan solid. ¹HNMR spectrum (25 °C, C₆D₆/CD₃CN): δ = 7.72 (m, 6H), 7.46 (m, 2H), 7.3-7.0 (m, 36H), 6.90 (t,

3H), 6.45 (d, 2H), 3.05 (br s, 2H). $^{13}\text{CNMR}$ spectrum (25 °C, $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): δ = 137.3, 136.9, 135.7, 133.9, 132.4, 132.3, 129.7, 129.7, 129.6, 125.9, 125.8, 121.8, 116.3, 114.2 $^{11}\text{BNMR}$ spectrum (25 °C, $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): δ = -6.32.

[*p*-BPh₃C₆H₄NHSiMe₂CpHMe₄][Li(THF)₄] (6-4f). To a solution of **6-4e** (0.50 g, 1.0 mmol) in 30 mL THF at -78 °C was added BuLi (0.52 mL, 1.3 mmol) and the solution was stirred for 10 min and then slowly warmed to room temperature over 15 min. After stirring for an additional 30 min, this solution was added to a solution of Me₄CpHSiMe₂Cl (0.29 g, 1.3 mmol) in 15 mL THF and the solution stirred for five hours. The solvent was then concentrated *in vacuo* to five mL, and 30 mL pentane was added. A greenish-yellow oil formed, and the supernatant solution was decanted away. The oil was washed twice with 20 mL hexanes and then dried *in vacuo* yielding **6-4f** (0.75 g, 80%) as a slightly gummy, yellow solid. $^1\text{HNMR}$ spectrum (25 °C, $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): δ = 7.65 (m, 6H), 7.42 (m, 2H), 7.08 (t, 6H), 6.89 (t, 3H), 6.57 (d, 2H), 3.48 (m, 16H), 3.22 (br s, 1H), 3.12 (br s, 1H), 1.88 (s, 6H), 1.62 (s, 6H), 1.50 (m, 16H), 0.02 (s, 6H). $^{13}\text{CNMR}$ spectrum (25 °C, $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): δ = 136.6, 135.3, 135.2, 125.8, 125.7, 125.6, 125.5, 121.4, 121.3, 115.2, 67.3, 26.2, 14.2, 11.1, 0.0. $^{11}\text{BNMR}$ spectrum (25 °C, $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): δ = -6.47.

Li(THF)₄ [(*p*-BPh₃C₆H₄NSiMe₂CpMe₄)Zr(NMe₂)₂] (6-4g). To a solution of **6-4f** (0.10 g, 0.13 mmol) in 10 mL C_6H_6 and two mL THF was added Zr(NMe₂)₄ (0.04 g, 0.13 mmol) and the solution stirred for six hours. The solvent was removed *in vacuo*, and the resulting solid was washed with 20 mL hexanes. The solid was dried *in vacuo* yielding **6-4g** (0.10 g, 65 %) as a yellow solid. $^1\text{HNMR}$ spectrum (25 °C, C_6D_6): δ = 7.60 (m, 6H), 7.34 (m, 2H), 7.05 (t, 6H), 6.84 (t, 3H), 6.55 (d, 2H), 3.58 (m, 16H), 2.78 (s, 12H), 2.30 (s, 6H), 2.18 (s, 6H), 1.75 (m, 16H), 0.02 (s, 6H).

$[p\text{-BPh}_3\text{C}_6\text{H}_4\text{NLiSiMe}_2\text{CpLiMe}_4][\text{Li}(\text{THF})_4]$ (**6-4h**). To a solution of **6-4f** (0.40 g, 0.60 mmol) in 30 mL THF at -78°C was added BuLi (0.72 mL, 1.8 mmol) and the yellow solution immediately became darker. The solution warmed to room temperature and stirred for eight hours. The red solution was concentrated to five mL *in vacuo* and 30 mL pentane was added. A yellow oil formed, and the supernatant solution was decanted away. The oil was washed twice with 20 mL pentane and solidified into a finely divided solid. The solid was filtered and dried *in vacuo* yielding **6-4h** (0.40 g, 97%) as a yellow solid. ^1H NMR spectrum (25°C , $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): $\delta = 7.65$ (m, 6H), 7.35 (m, 2H), 7.05 (t, 6H), 6.95 (t, 3H), 6.58 (d, 2H), 3.50 (m, 16H), 2.25 (s, 6H), 2.05 (s, 6H), 1.50 (m, 16H), 0.58 (s, 6H).

$[\text{Li}(\text{THF})_4][p\text{-BPh}_3\text{C}_6\text{H}_4\text{NSiMe}_2\text{CpMe}_4]\text{ZrCl}_2$ (**6-4i**). To a solution of **6-4h** (0.10 g, 0.14 mmol) in 10 mL THF at -78°C was added a solution of ZrCl_4 (0.03 g, 0.14 mmol) in 10 mL THF, and the solution was warmed to room temperature. The solution was stirred for three hours and then the solvent was concentrated *in vacuo* to approximately five mL. To this was added 20 mL pentane and a yellow oil precipitated. The supernatant solution was decanted away and the oil was dried *in vacuo* yielding **6-4i** (0.09 g, 75%) as a yellow solid. ^1H NMR spectrum (25°C , $\text{C}_6\text{D}_6/d^8\text{-THF}$): $\delta = 7.84$ (m, 6H), 7.42 (m, 2H), 7.10 (t, 6H), 6.90 (t, 3H), 6.58 (d, 2H), 3.51 (m, 16H), 1.90 (s, 6H), 1.70 (s, 6H), 1.53 (m, 16H), 0.03 (s, 9H), -0.06 (s, 6H). ^{11}B NMR spectrum (25°C , $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): $\delta = -6.29$.

$[\text{Li}(\text{THF})_4][p\text{-BPh}_3\text{C}_6\text{H}_4\text{NSiMe}_2\text{CpMe}_4]\text{ZrMe}_2$ (**6-4j**). To a solution of **6-4i** (0.3 g, 0.31 mmol) in 20 mL THF at -78°C was added a solution of MeMgBr (0.10 mL, 0.77 mmol) in Et_2O , and the solution warmed to room temperature. The solution stirred for eight hours and then was concentrated to approximately five mL *in vacuo*. To the solution was added 30 mL pentane

and a yellow oil precipitated. The supernatant was decanted away, and the oil dried *in vacuo* yielding **6-4j** (0.22 g, 78%) as a yellow solid. ^1H NMR spectrum (25 °C, $\text{C}_6\text{D}_6/\text{d}^8\text{-THF}$): δ = 7.28 (m, 6H), 6.96 (m, 2H), 6.80 (t, 6H), 6.65 (t, 3H), 6.10 (d, 2H), 3.58 (m, 16H), 2.13 (s, 6H), 1.96 (s, 6H), 1.55 (m, 16H), 0.45 (s, 6H), -1.70 (s, 6H).

***p*-Br-2,6-Me₂C₆H₂N(TMS)₂ (6-5a).** To a solution of *p*-bromo-2,6-dimethylaniline (4.10 g, 20.4 mmol) in 60 mL THF at -78 °C was added LDA (10.25 mL, 20.4 mmol) and the mixture stirred for 15 min. To this solution was added TMSCl (2.6 mL, 20.4 mmol), and the solution was stirred for 15 min. A second equivalent of LDA (10.25 mL, 20.4 mmol) was added, and the mixture stirred for 15 min before adding another equivalent of TMSCl (2.6 mL, 20.4 mmol). The solution was warmed to room temperature and stirred for two hours. The solvent removed *in vacuo*, and the residue was extracted twice with 30 mL pentane. The pentane was removed *in vacuo* yielding **6-5a** (5.02 g, 90%) as a white solid. ^1H NMR spectrum (25 °C, C_6D_6): δ = 7.10 (s, 2H), 1.99 (s, 6H), 0.02 (s, 18H). ^{13}C NMR spectrum (25 °C, C_6D_6): δ = 145.4, 139.3, 131.2, 117.0, 20.0, 2.5.

[*p*-BPh₃-2,6Me₂-C₆H₂N(TMS)₂][Li(THF)₄] (6-5b). To a solution of **6-5a** (1.0 g, 3.7 mmol) in 50 mL THF at -78 °C was added BuLi (1.47 mL, 3.7 mmol) and the solution was stirred for 30 min. This solution was added to a mixture of BPh₃ (0.89 g, 3.7 mmol) in 20 mL THF at -78 °C and the mixture stirred at -78 °C for two hours during which time, all solid dissolved. The mixture was then warmed to 25 °C and stirred for eight hours. The solvent was removed *in vacuo* and the resulting solid washed with 3 x 20 mL pentane and then dried *in vacuo* yielding **3b** (2.26 g, 85%) as a white solid. ^1H NMR spectrum (25 °C, $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): δ = 7.93 (br d, 6H), 7.55 (br s, 2H), 7.24 (t, 6H), 7.09 (t, 3H), 3.11 (m, 16H), 2.30 (s, 6H), 1.28 (m, 16H), 0.19 (s, 18H). ^{13}C NMR spectrum (25 °C,

$\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): $\delta = 140.8, 136.8, 136.5, 133.6, 126.8, 122.9, 68.1, 25.4, 21.0, 2.8$.

$^{11}\text{BNMR}$ spectrum (25°C , $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): $\delta = -6.40$.

[*p*-BPh₃-2,6-Me₂-C₆H₂N(TMS)₂] PPN (6-5c). To a solution of **6-5b** (0.35 g, 0.49 mmol) in acetonitrile was added PPNCl (0.28 g, 0.49 mmol) and a white solid immediately precipitated. The mixture was stirred for eight hours, the LiCl was filtered, and the acetonitrile was removed *in vacuo* yielding a white solid. The solid was washed with 15 mL H₂O and dried *in vacuo* yielding **6-5c** (0.39 g, 98%) as a white solid. $^1\text{HNMR}$ spectrum (25°C , $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): $\delta = 7.40 - 7.10$ (m, 36H), 7.00 (br m, 2H), 6.90 (t, 6H), 6.75 (t, 3H), 3.48 (m, 16H), 1.99 (s, 6H), 1.50 (m, 16H), -0.05 (s, 18H). $^{13}\text{CNMR}$ spectrum (25°C , $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): $\delta = 137.0, 136.9, 135.6, 133.9, 132.4, 132.3, 132.2, 129.8, 129.7, 129.6, 129.5, 129.5, 125.9, 125.8, 125.7, 125.7, 121.9, 116.5, 21.3, 5.2$. $^{11}\text{BNMR}$ spectrum (25°C , $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): $\delta = -6.42$.

[*p*-BPh₃-2,6-Me₂-C₆H₂NH₂][Li(NBu₃)₂] (6-5d). To a solution of **6-5b** (1.2 g, 1.8 mmol) in 20 mL THF was added a solution of Bu₄NF-H₂O (1.86 g, 7.2 mmol) in 5 mL THF, and the solution stirred for four days. The THF was then removed *in vacuo* and 15 mL benzene was added to the resulting oil. The mixture was stirred for two hours and then filtered. The benzene was removed *in vacuo* yielding **6-5d** (1.94 g, 82%) as a white solid. $^1\text{HNMR}$ spectrum (25°C , $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): $\delta = 7.84$ (m, 6H), 7.32 (m, 2H), 7.20 (t, 6H), 7.00 (t, 3H), 2.84 (dd, 12H), 2.05 (s, 6H), 1.30 (m, 24H), 0.90 (t, 18H). $^{13}\text{CNMR}$ spectrum (25°C , $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): $\delta = 166.0, 138.1, 136.8, 125.9, 121.9, 118.9, 53.3, 23.9, 19.9, 18.3, 13.8$.

[*p*-BPh₃-2,6-Me₂-C₆H₂NH₂] NBu₄ (6-5e). To a solution of **6-5c** (1.0 g, 0.96 mmol) in 20 mL THF was added a solution of Bu₄NF-H₂O (2.5 g, 9.6 mmol) in five mL THF, and the solution stirred for five days. The THF was then removed *in vacuo* and the resulting oil was washed with 30 mL water. The

brown, oily solid was dissolved in five mL THF and 30 mL pentane was added. An off-white solid was collected by filtration and dried *in vacuo* yielding **6-5e** (0.45 g, 78%) as an off-white solid. ^1H NMR spectrum (25 °C, $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): δ = 7.72 (m, 6H), 7.18 (m, 2H), 7.10 (t, 6H), 6.92 (t, 3H), 3.06 (br s, 2H), 2.44 (dd, 8H), 1.98 (s, 6H), 1.10 (m, 16H), 0.80 (t, 12H). ^{13}C NMR spectrum (25 °C, $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): δ = 136.9, 135.7, 125.9, 125.8, 125.8, 125.7, 121.8, 121.6, 58.8, 23.9, 19.8, 17.9, 13.4 ^{11}B NMR spectrum (25 °C, $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): δ = -6.42.

[*p*- BPh_3 -2,6- $\text{Me}_2\text{C}_6\text{H}_2\text{NHSiMe}_2\text{CpHMe}_4$] NBu_4 (**6-5f**). To a solution of **6-5e** (0.08 g, 0.13 mmol) in 30 mL THF at -78 °C was added BuLi (0.06 mL, 0.17 mmol) and the solution was stirred for 10 min and then slowly warmed to room temperature over 15 min. After stirring for an additional 30 min, this solution was added to a solution of $\text{Me}_4\text{CpHSiMe}_2\text{Cl}$ (0.06 g, 0.17 mmol) in 15 mL THF and the solution stirred for five hours. The solvent was then removed *in vacuo*, and the resulting oily solid washed with 20 mL pentane. The solid was dried *in vacuo* yielding **6-5f** as a yellow solid. ^1H NMR spectrum (25 °C, $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): δ = 7.55 (m, 6H), 7.14 (m, 2H), 7.00 (t, 6H), 6.82 (t, 3H), 3.10 (br s, 1H), 2.90 (br s, 1H), 2.50 (dd, 8H), 2.05 (s, 6H), 1.90 (s, 6H), 1.70 (s, 6H), 1.10 (m, 16H), 0.80 (t, 12H), 0.00 (s, 6H).

p-Br-2,6-*i*-Pr $_2\text{C}_6\text{H}_2\text{N}(\text{TMS})_2$ (**6-6a**). To a solution of *p*-bromo-2,6-diisopropylaniline (0.36 g, 1.4 mmol) in 60 mL THF at -78 °C was added LDA (0.94 mL, 1.4 mmol) and the mixture stirred for 30 min. To this solution was added TMSCl (0.18 mL, 1.4 mmol), and the solution was stirred for 30 min. A second equivalent of LDA (0.94 mL, 1.4 mmol) was added, and the mixture stirred for 30 min before adding another equivalent of TMSCl (0.18 mL, 1.4 mmol). The solution was warmed to room temperature and stirred for four hours. The solvent removed *in vacuo*, and the residue was extracted twice with 30 mL pentane. The pentane was removed *in vacuo* yielding **6-6a** (0.43 g,

76%) as a light red solid. ^1H NMR spectrum (25 °C, C_6D_6): δ = 7.31 (s, 2H), 3.39 (sept, 2H), 1.04 (d, 12H), 0.06 (s, 18H). ^{13}C NMR spectrum (25 °C, C_6D_6): δ = 149.9, 142.8, 127.5, 118.9, 28.0, 24.9, 2.7.

[*p*- BPh_3 -2,6-*i*- $\text{Pr}_2\text{C}_6\text{H}_2\text{N}(\text{TMS})_2$][$\text{Li}(\text{THF})_4$] (**6-6b**). To a solution of **6-6a** (0.75 g, 1.9 mmol) in 50 mL THF at -78 °C was added BuLi (0.75 mL, 1.9 mmol) and the solution was stirred for 30 min. This solution was added to a mixture of BPh_3 (0.45 g, 1.9 mmol) in 20 mL THF at -78 °C and the mixture stirred at -78 °C for two hours during which all solid dissolved. The mixture was then warmed to 25 °C and stirred for eight hours. The solvent was removed *in vacuo* and the resulting solid washed with 3 x 20 mL pentane and then dried *in vacuo* yielding **6-6b** (1.3 g, 97%) as a white solid. ^1H NMR spectrum (25 °C, C_6D_6): δ = 7.68 (br m, 6H), 7.38 (br m, 2H), 7.11 (t, 6H), 6.92 (t, 3H), 3.48 (m, 16H), 3.45 (sept, 2H), 1.50 (m, 16H), 1.15 (d, 12H), 0.14 (s, 18H). ^{13}C NMR spectrum (25 °C, C_6D_6): δ = 165.8, 142.2, 136.7, 135.5, 132.2, 125.9, 122.0, 67.9, 27.8, 25.7, 25.5, 2.8. ^{11}B NMR spectrum (25 °C, C_6D_6): δ = -6.32.

[*p*- BPh_3 -2,6-*i*- $\text{Pr}_2\text{C}_6\text{H}_2\text{N}(\text{TMS})_2$] PPN (**6-6c**). To a solution of **6-6b** (0.70 g, 0.82 mmol) in acetonitrile was added PPNCl (0.47 g, 0.82 mmol) and a white solid immediately precipitated. The mixture was stirred for eight hours, the LiCl was filtered, and the acetonitrile was removed *in vacuo* yielding a white solid. The solid was washed with 15 mL H_2O and dried *in vacuo* yielding **6-6c** (0.78 g, 87%) as a white solid. ^1H NMR spectrum (25 °C, C_6D_6 / CD_3CN): δ = 7.60 (m, 6H), 7.3-7.1 (m, 32H), 7.05 (t, 6H), 6.85 (t, 3H), 3.40 (sept, 2H), 1.10 (d, 12H), 0.05 (s, 18H). ^{13}C NMR spectrum (25 °C, C_6D_6 / CD_3CN): δ = 136.8, 133.9, 132.4, 132.3, 132.2, 129.7, 129.6, 129.5, 125.6, 125.5, 125.5, 121.8, 116.4, 27.8, 25.3, 2.8. ^{11}B NMR spectrum (25 °C, C_6D_6 / CD_3CN): δ = -6.23.

[*p*- BPh_3 -2,6-*i*- $\text{Pr}_2\text{C}_6\text{H}_2\text{NH}_2$][$\text{Li}(\text{NBu}_3)_4$] (**6-6d**). To a solution of **6-6b** (0.60 g, 0.54 mmol) in 20 mL THF was added a solution of $\text{Bu}_4\text{NF} \cdot \text{H}_2\text{O}$ (2.37 g, 5.4

mmol) in 5 mL THF, and the solution stirred for four days. The THF was then removed *in vacuo* and 15 mL benzene was added to the resulting oil. The mixture was stirred for two hours and then filtered. The benzene was removed *in vacuo* yielding **6-6d** as a brown oily solid. ^1H NMR spectrum (25 °C, C_6D_6): δ = 7.90 (m, 6H), 7.45 (br s, 2H), 7.22 (t, 6H), 7.10 (t, 3H), 3.20 (s, 2H), 2.98 (dd, 12H), 1.30 (m, 24H), 1.28 (d, 12H), 0.92 (t, 18H). ^{13}C NMR spectrum (25 °C, C_6D_6): δ = 166.4, 137.3, 135.4, 131.5, 129.7, 126.2, 125.9, 58.2, 28.8, 24.2, 23.6, 20.0, 14.1.

[*p*-BPh₃-2,6-*i*-Pr₂C₆H₂NH₂] NBu₄ (**6-6e**). To a solution of **6-6c** (0.60 g, 0.54 mmol) in 20 mL THF was added a solution of Bu₄NF·H₂O (2.37 g, 5.4 mmol) in 5 mL THF, and the solution stirred for four days. The THF was then removed *in vacuo* and the resulting oil was washed with 30 mL water. The brown, oily solid was dissolved in five mL THF and 30 mL pentane was added. An off-white solid was collected by filtration and dried *in vacuo* yielding **6-6e** as an off-white solid. ^1H NMR spectrum (25 °C, $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): δ = 7.72 (m, 6H), 7.18 (m, 2H), 7.10 (t, 6H), 6.92 (t, 3H), 3.30 (sept, 2H), 3.06 (br s, 2H), 2.44 (dd, 8H), 1.75 (s, 6H), 1.28 (d, 12H), 1.10 (m, 16H), 0.80 (t, 12H). ^{13}C NMR spectrum (25 °C, $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): δ = 136.9, 135.7, 125.9, 125.8, 125.8, 125.7, 121.8, 121.6, 58.8, 23.9, 19.8, 17.9, 13.4 ^{11}B NMR spectrum (25 °C, $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$): δ = -6.42.

X-ray Structure Determination of **6-1b**

Data were collected at 173 K on a Siemens SMART PLATFORM equipped with A CCD area detector and a graphite monochromator utilizing MoK α radiation (λ = 0.71073 Å). Cell parameters were refined using up to 5645 reflections. A hemisphere of data (1381 frames) was collected using the ω -scan method (0.3° frame width). The first 50 frames were remeasured at

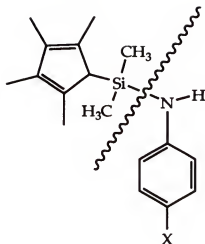
the end of data collection to monitor instrument and crystal stability (maximum correction on I was $< 1\%$). Empirical absorption corrections were applied based on the entire data set.

The structure was solved by the Direct Methods in *SHELXTL5*, and refined using full-matrix least squares. The non-H atoms were treated anisotropically and all of the hydrogen atoms were obtained from a Difference Fourier map and refined without constraints. 381 parameters were refined in the final cycle of refinement using 4411 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 2.67 and 6.32%, respectively. Refinement was done using F^2 .

Results and Discussion

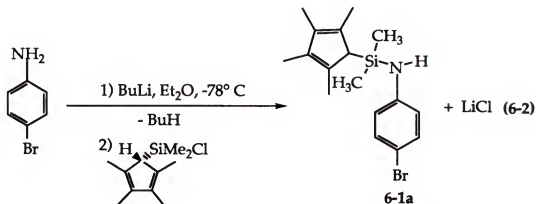
We have recently been interested in methods for preparing covalently linked, borate-containing transition metal complexes, and in our studies have found that the borate can be prepared when the ligand being functionalized is already bound to an 18 electron metal species. However, when high oxidation state early transition metals are used, the reaction can lead to complex, intractable mixtures. This is because the method we have chosen for preparing a B-C bond, the halo-lithium exchange reaction, involves the use of a strongly basic and nucleophilic alkyl lithium reagent which can react with the electrophilic metal center. Therefore, we looked for other methods for preparing a borate-containing ligand before coordination of the ligand to the metal.

The new class of constrained geometry ligands (CpSiNR) initially developed by Bercaw's group offers an excellent opportunity to prepare these borate-containing ligands. The ligand is made up of two general parts; a Cp ligand with a silyl linker, and an amine. Therefore, we chose to prepare

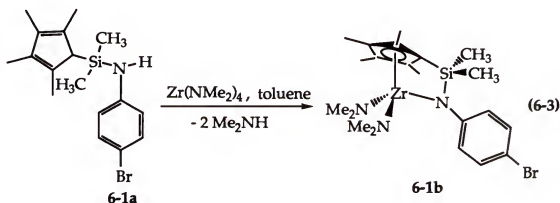


borate-containing aniline derivatives which we could then react with a Cp-Si-Cl in order to prepare borate-containing ligands.

The synthesis of the half-sandwich borate-containing zirconocene, **6-1f**, (Scheme 6-1) is accomplished starting with *p*-bromoaniline. The aniline is easily deprotonated by BuLi in diethyl ether at -78°C , a temperature at which halo-lithium exchange does not occur in Et₂O. The anilide reacts with the Si-Cl bond of Me₄CpHSiMe₂Cl, (equation 6-2) and LiCl is displaced. The



new ligand, **6-1a**, is soluble in hydrocarbon solvents, and is easily separated from the lithium chloride by filtration. Removal of solvent by evaporation leads to the isolation of **6-1a** as a yellow oil. The protonated ligand reacts with $\text{Zr}(\text{NMe}_2)_4$ and eliminates two equivalents of dimethylamine (equation 6-3), yielding the zirconium complex **6-1b**. This reaction works well in both Et_2O



or toluene, and single crystals of the zirconium complex can be grown from cold hexanes or by slow evaporation of a concentrated solution in benzene. The zirconium complex **6-1b** is formally a 12 electron complex, but if one considers the available π -electrons available on each of the three amide ligands, one can conceivably consider the complex to be an 18 electron species. With this in mind, halo-lithium exchange was attempted on the bis-dimethylamido zirconium complex with BuLi in THF at -78°C in an attempt to prepare a borate with the pre-coordinated ligand. However, as one might expect, donation by the amide ligands is not significant enough to deactivate the electrophilic metal center from attack by such a strong nucleophile as BuLi , and reactivity at the metal center is observed.

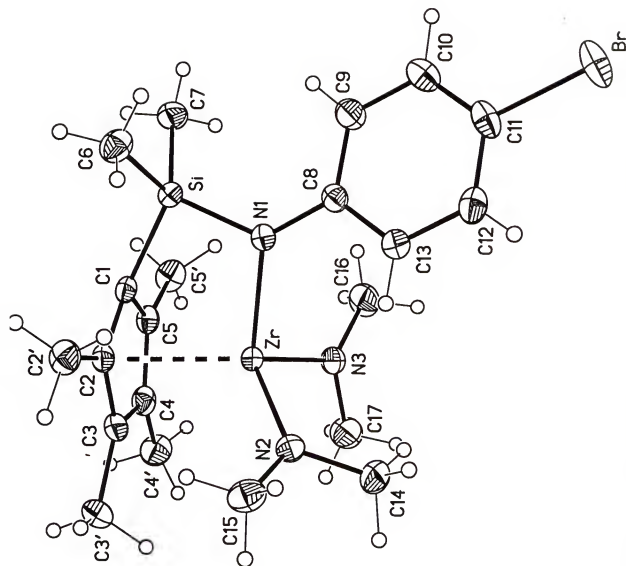


Figure 6-1. Thermal ellipsoid plot of 6-1b with thermal ellipsoids at the 50% probability level.

The crystal structure (Figure 6-1) of the zirconium complex **6-1b** was determined, and the structure around the metal is pseudo-tetrahedral. Table 6-1 gives some relevant bond lengths and angles. The strain imparted by the linked Cp-Si-N bonds is most evident in the C1-Si-N1 angle, which is 94.8°. Other evidence for the strain in the molecule is the lengthened Zr-N1 bond, which is almost 0.1 Å longer (2.150Å) than the other two Zr-N bonds (avg. 2.06Å). A slight bend is present in the Cp ring, with the carbon linked to the silyl group slightly closer to the metal center than the other carbons of the ring (Table 6-1).

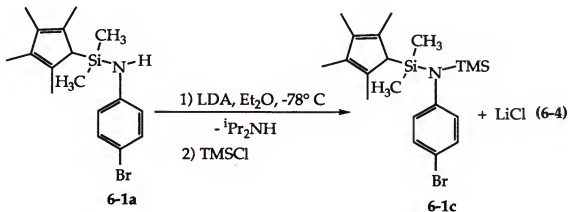
Table 6-1. Selected bond lengths and angles for **6-1b**.

bond lengths (Å)		bond angles (deg)	
Zr-N1	2.150 (2)	C1-Si-N1	94.77 (9)
Zr-N2	2.082 (2)	Si-N1-C8	128.11 (14)
Zr-N3	2.050 (2)	Si-N1-Zr	105.08 (8)
Zr-C1	2.466 (2)	N3-Zr-N2	104.18 (7)
Zr-C2	2.558 (2)	N3-Zr-N1	102.48 (7)
Zr-C3	2.593 (2)	N1-Zr-N2	112.26 (7)
Zr-C4	2.551 (2)		
Zr-C5	2.503 (2)		
Si-N1	1.740 (2)		
Si-C1	1.880 (2)		

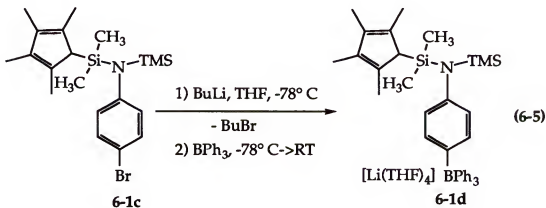
Table 6-2. Crystal data and structure refinement for **6-1b**.

Empirical formula	C ₂₁ H ₃₄ Br N ₃ Si Zr
Formula weight	527.73
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 10.2857(2) Å α = 62.352(1)° b = 11.4076(1) Å β = 77.551(1)° c = 11.6100(1) Å γ = 84.566(1)°
Volume, Z	1178.32(3) Å ³ , 2
Density (calculated)	1.487 Mg/m ³
Absorption coefficient	2.224 mm ⁻¹
F(000)	540
Crystal size	0.27 × 0.19 × 0.04 mm
Theta range for data collection	2.02 to 27.50 deg.
Limiting indices	-13 ≤ h ≤ 7, -15 ≤ k ≤ 14, -14 ≤ l ≤ 14
Reflections collected	7901
Independent reflections	5184 [R(int) = 0.0190]
Absorption correction	Empirical
Min. & Max. Transmissions	0.662, 0.935
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5181 / 0 / 381
Goodness-of-fit on F ²	0.995
Final R indices [I > 2σ(I)]	R1 = 0.0267, wR2 = 0.0632 [4411]
R indices (all data)	R1 = 0.0345, wR2 = 0.0668
Extinction coefficient	0.0061(6)
Largest diff. peak and hole	0.537 and -0.396 e•Å ⁻³

Further chemistry can be accomplished with the ligand **6-1a**. In order to prepare a borate from the protonated ligand using the halo-lithium exchange reaction, the amine must be protected with a TMS group. Thus, the aniline can be deprotonated with lithium diisopropylamide at -78°C , and the resulting anilide trapped with TMSCl (equation 6-4), yielding the TMS-protected ligand **6-1c**. Once protected, halo-lithium exchange is accomplished

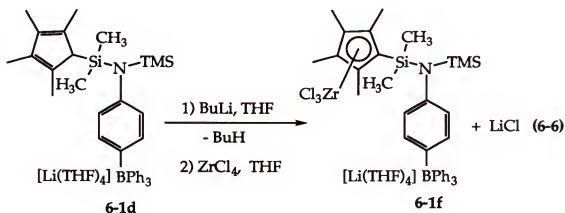


by the addition of BuLi to the protected ligand at -78°C in THF, and the resulting lithiate trapped with BPh_3 (equation 6-5). The borate, **6-1d**, is easily isolated by the addition of a hydrocarbon solvent such as pentane or hexanes.

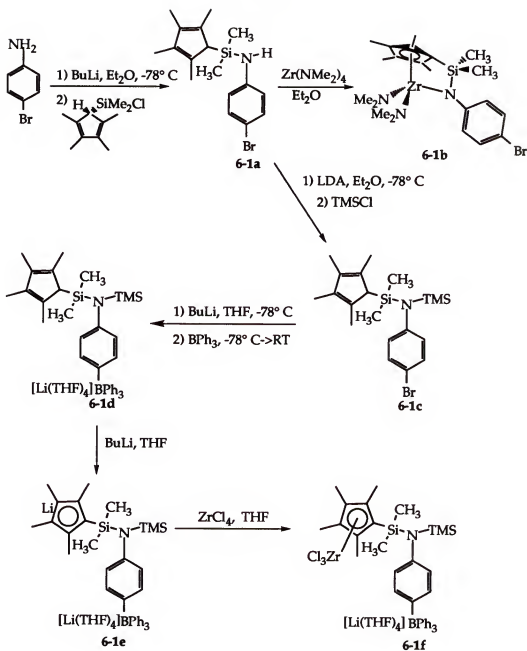


The insoluble borate precipitates from the solution as a red oil, and the solvent is then decanted away.

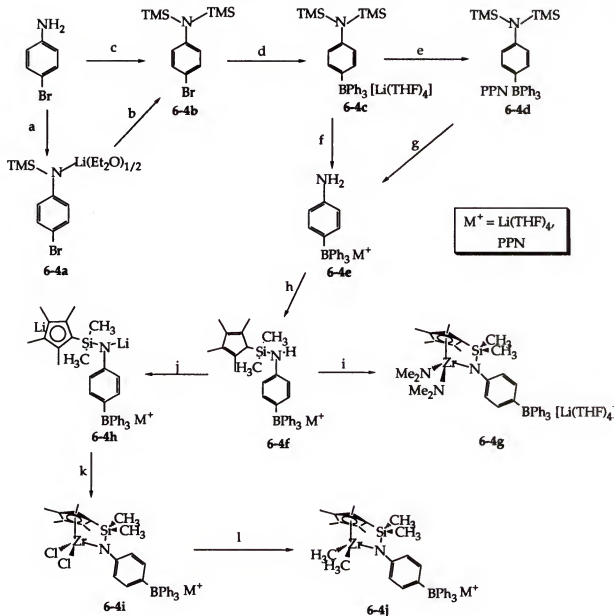
Deprotection of the TMS-protected ligand, **6-1d**, is not possible because both Si-N bonds in the ligand are susceptible to cleavage under similar conditions. However, the TMS-protected ligand can be used as a non-chelating Cp ligand, and deprotonation of the Cp group, followed by addition of ZrCl_4 in THF yields (equation 6-6) the borate-containing half-sandwich zirconium complex **6-1f**. It is noteworthy that the TMS-protected ligand



bound to the ZrCl_3 fragment does not undergo an intra-molecular reaction to eliminate TMSCl and form a chelated, constrained geometry complex. Green and coworkers^{102b} found that under similar conditions, a TMS protected primary amine linked through a hydrocarbon chain to a bound Cp ligand, undergoes an intramolecular reaction resulting in a niobium chelated Cp-imido complex. It is likely that the much smaller chain length, and more sterically hindered protected aniline in our system reduces the likelihood for the intra-molecular attack.

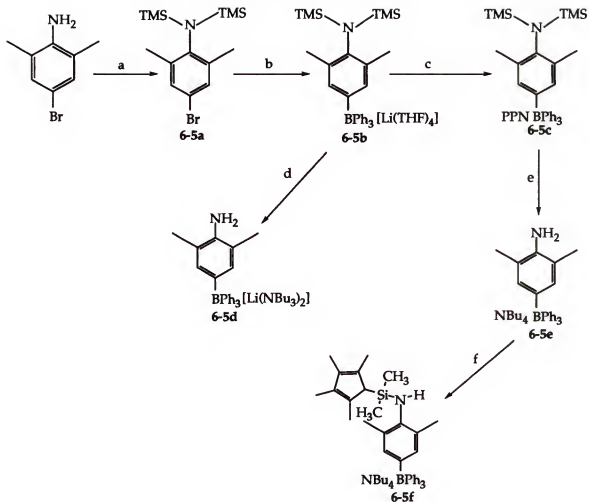


Scheme 6-1



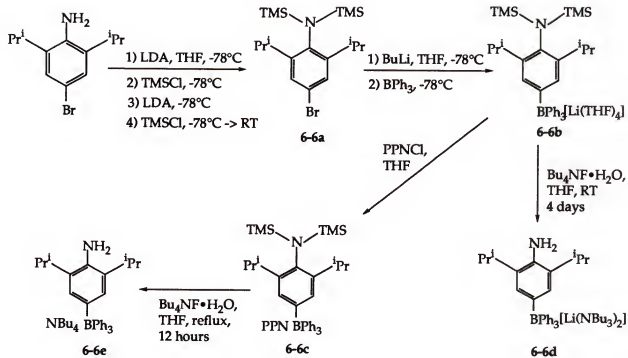
Scheme 6-2

Reaction conditions: (a) 1) BuLi, Et₂O, -78°C, 2) TMSCl, -78°C, 3) BuLi, -78°C → RT; (b) TMSCl, THF, RT; (c) 1) LDA, THF, -78°C, 2) TMSCl, 3) LDA, 4) TMSCl, -78°C → RT; (d) 1) BuLi, THF, -78°C, 2) BPh₃, -78°C → RT; (e) PPNCl, THF, RT; (f) MeOH, RT, 4 days; (g) THF/H₂O, reflux, 8 hours; (h) 1) BuLi, THF, -78°C → RT, 2) Me₄CpHSiMe₂Cl; (i) Zr(NMe₂)₄, toluene, reflux; (j) 3 BuLi, THF, -78°C → RT; (k) ZrCl₄, THF, -78°C → RT; (l) 2 MeMgBr, THF, -78°C → RT.

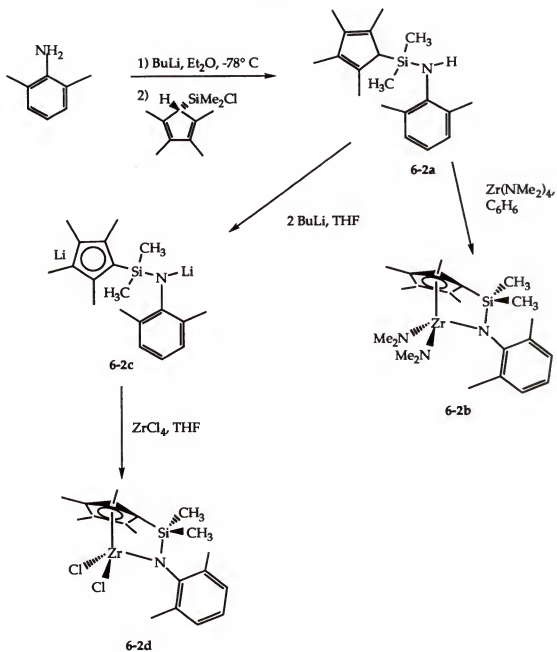


Scheme 6-3

Reaction conditions: (a) 1) LDA, THF, -78°C, 2) TMSCl, 3) LDA, 4) TMSCl, -78°C → RT; (b) 1) BuLi, THF, -78°C, 2) BPh₃, -78°C → RT; (c) PPNCl, THF, RT; (d) 6 Bu₄NF·H₂O, THF, RT, 4 days; (e) 6 Bu₄NF·H₂O, THF, reflux, 12 hours; (f) 1) BuLi, THF, -78°C → RT, 2) Me₄CpHSiMe₂Cl.



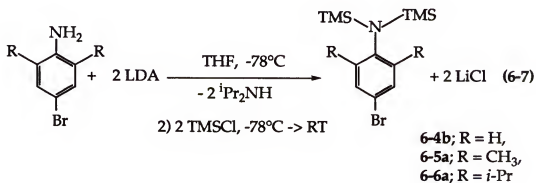
Scheme 6-4



Scheme 6-5

In order to prepare chelating, borate-containing ligands, we prepared a series of new, borate-containing anilines and examined the application of these anilines to the preparation of CpSiNR type ligands. We chose three aniline precursors, *p*-bromoaniline, *p*-bromo-2,6-dimethylaniline, and *p*-bromo-2,6-diisopropylaniline for our study. In order to prepare *p*-triphenylborate derivatives from these, protection of the amine protons was required. We chose TMS protecting groups because of their stability to strong bases and because they can be removed without the use of strong acids, to which borates are sensitive.¹⁰⁵

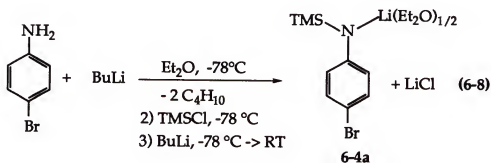
The protection of the three anilines, *p*-bromoaniline (Scheme 6-2), *p*-bromo-2,6-dimethylaniline (Scheme 6-3), and *p*-bromo-2,6-diisopropylaniline (Scheme 6-4), is most easily accomplished in THF by the stepwise addition of one equivalent of lithium diisopropylamide (LDA) followed by the addition of one equivalent of TMSCl. This procedure is repeated, and the fully protected anilines are achieved (equation 6-7). It is possible to add two equivalents of LDA at once, followed by two equivalents of TMSCl since



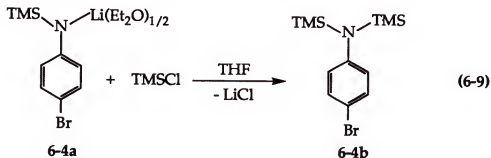
LDA is a non-nucleophilic base, but cleaner products are obtained after the stepwise addition, especially in the preparation of the protected

diisopropylaniline, **6-6a**. BuLi can also be used as the base if the reaction is done in Et₂O at -78°C. The first addition, followed by addition of TMSCl, results in the formation of the expected mono-TMS aniline derivative.

However, the addition of a second equivalent of BuLi, followed by excess TMSCl leads only to the mono-TMS anilide salt **6-4a**, which shows no reactivity toward TMSCl (equation 6-8). If the Et₂O is removed *in vacuo* and the resulting solid redissolved in THF, addition of TMSCl does lead to the

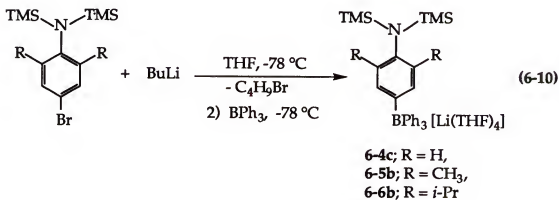


expected bis-TMS aniline compound **6-4b** (equation 6-9). This lack of reactivity of the Et₂O soluble mono-TMS anilide may be due to a dimeric structure which is proposed on the basis that the evaporation of Et₂O from the mono-TMS anilide leads exclusively to a salt containing only 1/2 Et₂O. This dimer may be too hindered to be a good nucleophile, however, in the

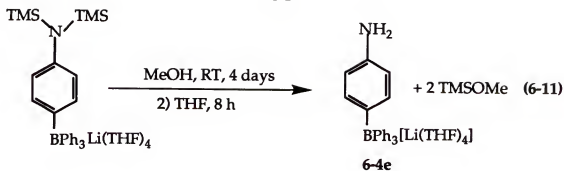


presence of the more polar THF solvent, the dimer is broken up into a monomeric anilide, which is again nucleophilic.

The relative ease at which the sterically hindered *p*-bromo-2,6-diisopropylaniline is deprotonated and trapped by TMSCl is somewhat surprising considering the large steric bulk of the two isopropyl groups. At -78°C in THF, the first deprotonation by LDA and trapping by TMSCl occurs almost instantaneously. The second deprotonation also occurs almost instantly, and the protection occurs within 1/2 hour as the solution warms to room temperature. Bromo-lithium exchange is readily performed in THF at -78 °C on the protected anilines, **6-4b**, **6-5a**, and **6-6a** (equation 6-10), with BuLi, and the subsequent phenyllithium complexes are trapped by triphenylboron (BPh₃) yielding the lithium salts, **6-4c**, **6-5b**, and **6-6b**, of the protected *p*-boratoanilines.



Deprotection of the borated anilines proved to be more difficult than expected. The Si-N bonds are surprisingly strong, and methanolysis of the non-alkylated TMS-protected aniline, **6-4c**, requires at least two to four days reaction time at room temperature to fully deprotect the anilines (equation 6-11). Heating the methanol solutions above 45° C leads to relatively little

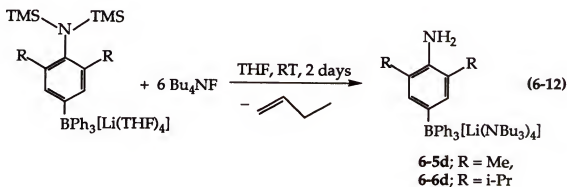


increase in the reaction rate and slow decomposition of the borate moiety. The methanol used for the deprotection was used as received, and no additional drying was done, which may explain the varying reaction times needed for the deprotection. Fortunately, very little decomposition of the borate occurs after four days in methanol at room temperature. Removal of the methanol *in vacuo*, followed by addition and removal of THF twice, leads to the replacement of methanol from the lithium coordination sphere with two to four THF ligands. Evacuation of the reaction flask overnight removes any residual methanol, which is important since the following steps require the use of strongly basic lithium alkyls.

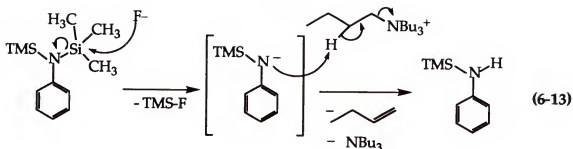
The deprotection of **6-4c** was also attempted using water, but the deprotected products were isolated in poor yield following substantial decomposition of the borate group, and the Li ion consistently contained two equivalents of bound water in its coordination sphere. The water proved impossible to remove, and its presence led to continued decomposition of the borate. Considering the blue color of the decomposition product, the sensitivity is probably due to the increased acidity of the ligated H_2O molecules, leading to oxidation of the aniline compound.

The TMS-protected *p*-borato-2,6-dialkylaniline derivatives **6-5b** and **6-6b** are too sterically hindered to be deprotected by methanolysis, and

decomposition of the borate occurred before complete deprotection in methanol could be accomplished. All of the aniline-borate derivatives appear to be more susceptible to decomposition by Bronsted-Lowry acids than traditional tetra-symmetric borates, and the enhanced acidity of methanol, when coordinated to a lithium ion, appears to be sufficiently strong to slowly degrade the borate moiety. To deprotect the sterically-hindered 2,6-dialkylated aniline derivatives, tetrabutylammonium fluoride (Bu_4NF) was used (equation 6-12). Corey and coworkers¹⁰⁶ first used this THF soluble, non-acidic deprotecting agent for TMS-protected alcohols. The deprotection of the

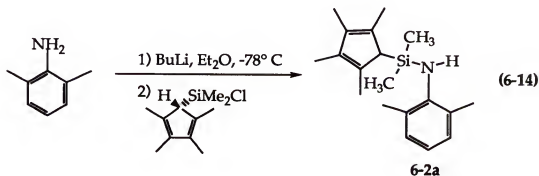


aniline derivative is driven by the formation of the extremely strong Si-F bond (582 KJ/mol) and the subsequent evaporation of the low-boiling TMS-F product. The anilide intermediate then deprotonates a butyl group of the Bu_4N^+ , leading to loss of 1-butylene and tributylamine (equation 6-13). This reaction can be done in THF or in a THF / MeOH solution, however the reaction appears to work best in THF with at least four equivalents of Bu_4NF . The only drawback of this method is the high boiling point and strong Lewis basicity of the resulting tributylamine, which displaces THF in the lithium ion coordination sphere. This results in poor crystallizability of the borate salt



6-6d, which is isolated as an oil. In attempts to avoid this problem, ammonium chloride (NH_4Cl) and ammonium fluoride (NH_4F) were used as deprotecting agents, however both salts proved too acidic and led to decomposition of the borate moiety.

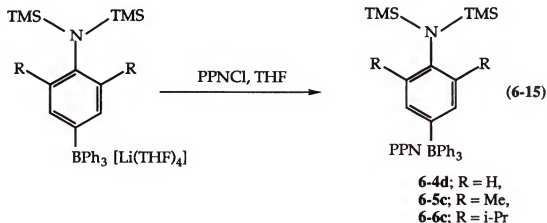
Unfortunately, the tributylamine ligands on the Li have a strong effect on the reactivity of the borato-anilines, and further chemistry could not be accomplished with these compounds. The 2,6-dialkylated-boratoanilines can be deprotonated by BuLi, however addition of $\text{CpMe}_4\text{HSiMe}_2\text{Cl}$ does not lead to the expected silyl-bridged Cp-amido ligands. Instead, no reactions are observed and the original Li anilides are recovered. This reactivity was unexpected with the 2,6-dimethylaniline derivative, since the non-borated 2,6-dimethylanilide reacts cleanly with $\text{CpMe}_4\text{HSiMe}_2\text{Cl}$ to yield the expected product (equation 6-14). Thus, it is assumed that the $\text{Li}(\text{NBu}_3)_2$



counterion is playing a role in the reduced reactivity, and probably interacting with the anilide anion. Therefore, we attempted to remove the $\text{Li}(\text{NBu}_3)_2$ by a number of methods.

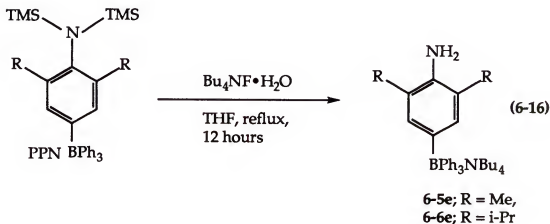
Ion exchange with bis-triphenylphosphoranylidene chloride (PPNCl) and NBu_4Cl does not occur, and each leads to eventual decomposition of the borate. This lack of exchange is probably due to the steric congestion around the small Li ion by the lipophilic butyl groups, making it difficult for LiCl to form. Addition of a large excess of LiCl in THF, to displace the $\text{Li}(\text{NBu}_3)_2$, also leads to decomposition of the borate. Displacement of the NBu_3 ligands was attempted with N,N,N',N' -tetramethylethylenediamine (TMEDA), THF, 1,2-dimethoxyethane (DME), and CH_3CN to no avail. The THF ligands bound to the Li ion of the TMS-protected aniline-borates can be exchanged with the chelating ligand TMEDA before deprotection, however deprotection of the anilines with Bu_4NF leads to substitution of the TMEDA with NBu_3 . This was surprising considering the chelating nature of TMEDA and the expected similarity in Lewis basicity of the two trialkylamines.

However, if the $\text{Li}(\text{THF})_4$ ion is exchanged by the addition of PPNCl (equation 6-15), before the deprotection is attempted, the NBu_3 has no Li to which to bind, and can be washed away after the reactions are complete.



In this manner, the isolation of borates without any NBu_3 was achieved. However, the borates were not isolated as PPN salts, but rather as NBu_4^+ salts, since the PPN was displaced by the NBu_4 cation.

The PPN salt of the TMS-protected, non-alkylated aniline borate (equation 6-16) was also prepared (**6-4d**), and this salt showed increased moisture stability over the Li salt **6-4c**, and can actually be deprotected

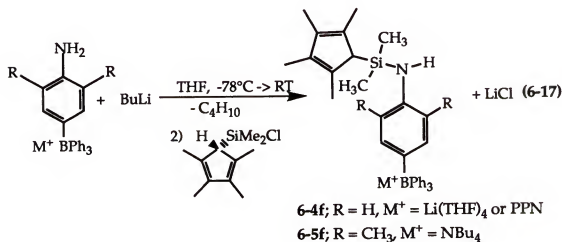


relatively quickly (overnight) by a mixture of THF and water. Apparently, like most tetraarylborates, the aniline borates are not water sensitive, but when the Li ion is present, water can coordinate to the metal, increasing its acidity. These borates, like most tetraarylborates are acid sensitive, and the increased acidity of the bound water is sufficient to degrade the borate.

Once the new borate-containing anilines were prepared, we examined the application of these compounds to the synthesis of the ligands. The groups of Herrmann^{102a,102f,102g,102i} and Petersen^{102c} have prepared CpSiNR ligands using both the metathetical method of reaction with metal chlorides and anionic ligands, and the addition of two equivalents of the aniline. In the second method, the second aniline is used to remove the acidic proton on

the amine after nucleophilic attack at the silicon has taken place. However, this method is not suitable when borate-containing anilines are used for three reasons; (1) the borates decompose in the presence of acids such as trialkylammonium chlorides, (2) the borate-aniline is tedious to prepare so it would be a waste, and (3) it is very difficult to separate two different borate compounds. Therefore, we focused on the metathetical method for preparing the ligands.

The borate-containing silyl-amide ligands **6-4f**, and **6-5f**, can be prepared by deprotonating the *p*-borato-aniline derivatives, **6-4e** or **6-5e**, with one equivalent of BuLi in THF (equation 6-17), followed by reaction with Me₄CpHSiMe₂Cl. This reaction is only possible because of the fortuitous

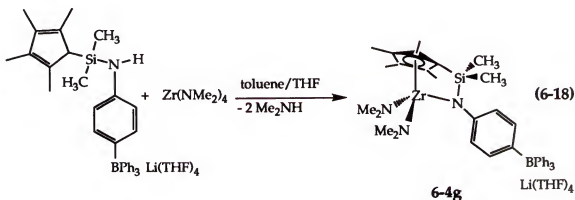


preference of the anilide toward nucleophilic attack at the Si-Cl bond, as opposed to deprotonation of the acidic Cp-proton. With the tetramethyl Cp ligand, the proton is kinetically inert due to the presence of the bulky methyl and dimethylsilyl groups. This preference is mentioned in the original paper by Bercaw and coworkers^{11b} discussing the new CpSiNR ligands, however it

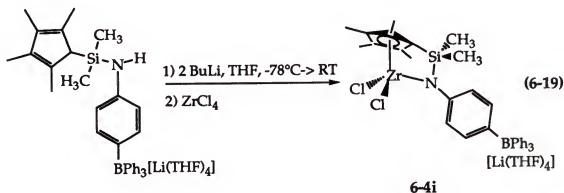
is truly understated when they comment that "It is convenient that the preferential reaction is between lithium tert-butylamide and the [Si-Cl] of (C₅Me₄H)SiMe₂Cl rather than deprotonation of the substituted cyclopentadiene." Indeed, without this preference, none of these borate-containing ligands could be prepared, since it is virtually impossible to separate mixtures of two borate-containing products.

One difficulty with all of the borate-containing complexes is the relative insolubility imparted by the tetraphenylborate moiety. Therefore, almost all reactions involving the borates must be done in THF, or other polar solvents. Fortunately, the borate compounds are relatively easy to purify, since they precipitate out of THF with the addition of hydrocarbon solvents. However, they usually precipitate out as oils, and only after all excess THF has been removed either under vacuum or by successive washings by the hydrocarbon solvents do they begin to solidify.

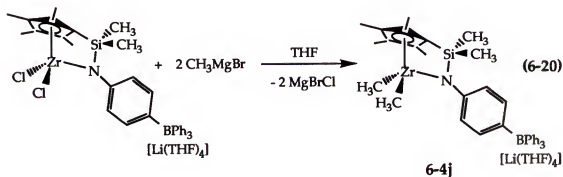
Once the borate-containing ligand **6-4f** is prepared, it can be used in two manners to prepare zirconium complexes. The protonated ligand undergoes amine elimination with Zr(NMe₂)₄ in a mixture of toluene/THF to yield the bis-dimethylamido zirconium complex **6-4g** (equation 6-18). Otherwise, the ligand can be deprotonated with two equivalents of BuLi in THF yielding the



tri-anionic ligand **6-4h**, which reacts with ZrCl_4 in THF to yield the zirconium dichloride complex **6-4i** (equation 6-19). The ligand is most easily worked with after deprotonation by BuLi , since the protonated ligand is an oily,



gummy solid, and therefore is difficult to manipulate. However, the deprotonated tri-anionic ligand is a fine powder that is easy to work with and is quite stable when kept under a nitrogen atmosphere. Finally, the dimethyl zirconium complex **6-4j**, can be prepared from the zirconium dichloride complex using typical conditions used for the synthesis of dimethyl metallocenes (equation 6-20). The reaction of two equivalents of MeMgBr with the dichloride complex **6-4i** produces the dimethyl zirconium complex, **6-4j**.

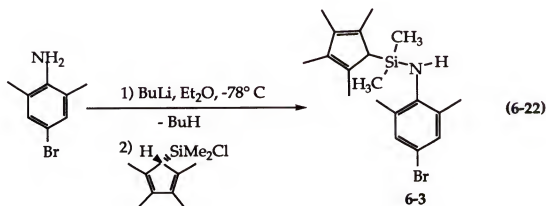
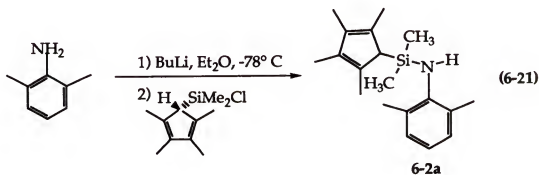


The synthesis of the related ligands derived from the 2,6-dialkylated anilines was also attempted and the synthesis of the 2,6-dimethyl substituted ligand was successfully prepared. Further chemistry with that ligand has not yet been attempted, but its ability to prepare metal complexes is expected to be similar to the non-alkylated system. The synthesis of the 2,6-diisopropyl derivative of the ligand has not yet been successful. This appears to be due to reduced nucleophilicity due to the bulky diisopropyl groups making the rate of deprotonation of the Cp proton rival that of nucleophilic attack. The result is a mixture of products that are difficult to separate. Attempts to prepare this ligand are continuing to be examined, and it is believed that with the proper reaction conditions, metal complexes containing this ligand will also be successfully achieved. However, similar chemistry was also accomplished with similar, non-borated anilines, and the results of this study will be discussed next.

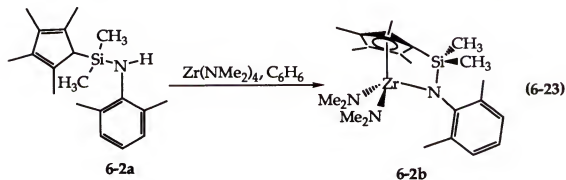
One problem with constrained geometry (CpSiNR) ligands is that they do not offer any stereocontrol of higher α -olefins due to such a large coordination site at the active metal center. One way to solve this problem is the synthesis of a CpSiNR ligand that contains bulky groups close to the metal center. Our studies of new anilines led us to examine the synthesis of metal complexes containing anilines with bulky alkyl groups in the 2- and 6-position. Alkyl groups in these positions should lie close to the active site and might aid in stereospecific coordination and polymerization of higher α -olefins.

The synthesis of CpSiNR ligands containing 2,6-dimethyl- and 2,6-diisopropylanilines were attempted, and the synthesis of the 2,6-dimethyl derivative was successful. If 2,6-dimethylaniline or *p*-bromo-2,6-dimethylaniline are deprotonated with BuLi in THF at -78°C, the resulting

anilides will react with $\text{Me}_4\text{CpHSiMe}_2\text{Cl}$ yielding the new dimethylaniline (equations 6-21 and 6-22) ligand derivatives **6-2a** and **6-3**. Ligand **6-2a** reacts

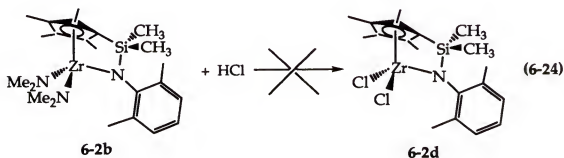


with $\text{Zr}(\text{NMe}_2)_4$, undergoing amine elimination to yield the bis-dimethylamido zirconium complex **6-2b** (equation 6-23). This complex, like

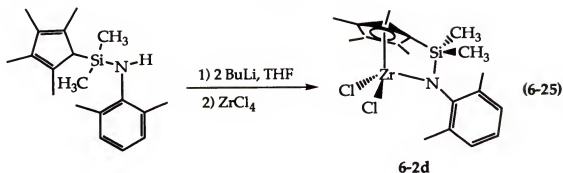


6-1b, also recrystallizes well from hexanes or benzene, and single crystals can be obtained.

Recently, Petersen and coworkers²² have reported that NEt_3HCl or HCl can be used to convert bis-dimethylamido complexes of zirconium to dichloride complexes, and this method was attempted for the conversion of **6-2b** to the dichloride complex **6-2d** (equation 6-24). The addition of 2.5 equivalents of HCl to **6-2b** in Et_2O yielded a complex mixture of products that



could not be separated. The reason for this different reactivity has not yet been determined, but it may be related to the different amine ligand, which in our case is an aryl amine, and in the Petersen case is an alkyl amine. Therefore, the metathetical method for preparing the zirconium complex was applied, and the protonated ligand **6-2a** was deprotonated with two equivalents of BuLi , forming the dianion **6-2c**. This reacts with ZrCl_4 in THF to yield the dichloride complex **6-2d** (equation 6-25).



Similar chemistry was attempted with 2,6-diisopropylaniline, but the reaction, like that with the borates, gave mixtures of products. Reaction products of the reaction between the anilide and $\text{Me}_4\text{CpHSiMe}_2\text{Cl}$ showed two separate aniline products, one of which appears to be the diisopropylaniline starting material. New reaction conditions are presently being examined, and it is expected that this ligand will also be successfully synthesized.

CHAPTER 7
SYNTHESIS OF DIIMINE LIGANDS AND LIGAND PRECURSORS
FOR THE DEVELOPMENT OF ZWITTERIONIC, LATE
TRANSITION METAL DIIMINE CATALYSTS

Introduction

The recent reports by the Brookhart group, that late-transition metal diimine catalysts with Pd and Ni polymerize ethylene with various degrees of branching, has produced a great deal of interest in the chemical community. These systems take advantage of bulky alkyl groups in the 2- and/or 6-position of the anilines of the diimine ligands, which do not allow associative displacement of bound polymer-containing olefins. This leads to practically living polymer systems, since the active catalyst retains the growing polymer even in its resting state. The synthesis of a living polymer system allows the possibility of the formation of block co-polymers, which are not possible with traditional Ziegler catalysts or homogeneous catalysts.

We have developed a series of new triphenylborate-containing anilines, including *p*-triphenylboratoaniline, *p*-triphenylborato-2,6-dimethylaniline, and *p*-triphenylborato-2,6-diisopropylaniline, and these borate-containing anilines appear to be useful precursors for the synthesis of borate-containing diimine ligands. The preliminary studies on the synthesis of these ligands will be discussed.

Experimental Section

General Considerations

All manipulations were performed under Ar by using standard Schlenk techniques or under N₂ in a Vacuum Atmospheres glove box unless otherwise noted. Glassware was oven dried prior to use. Solvents were distilled prior to use and stored over 4-Å molecular sieves in sealed bulbs under Ar. Diethyl ether and tetrahydrofuran were dried by distillation from Na/benzophenone ketyl. Pentane was dried by distillation from Na. NMR solvents were purchased from Cambridge Isotopes and were dried over 4-Å molecular sieves and not further purified. 2,6-Dimethylaniline, 2,6-diisopropylaniline, and 2,3-butadione were purchased from Aldrich and used as received. Methanol was purchased from Fisher and not further dried. All aniline borates and (tmeda)PdMe₂ were prepared according to literature methods.

¹H and ¹³C NMR spectra were obtained by using either a Varian VXR-300, Gemini-300, or G.E. QE-300 spectrometer. ¹¹B NMR spectra were obtained on a Varian VXR-300 spectrometer.

Procedures (ligands).

2-Phenylimino-3-butanone (1a). 2,3-Butadione (48 mL, 549 mmol) was added to aniline (1.0 mL, 11.0 mmol) and the solution stirred for six hours. The reddish solution was evacuated through a -78°C trap to isolate unreacted butadione. The crude product was dissolved in 10 mL benzene and 30 mL pentane was slowly added, precipitating an orange oil. The solution was decanted from the oil and the solvent removed *in vacuo* yielding **1a** as an

orange liquid (1.60 g, 91.4%) ^1H NMR (C_6D_6 , 25°C) δ = 7.12 (t, 2H, m-Ph), 6.92 (t, 1H, p-Ph), 6.58 (d, 2H, o-Ph), 2.31 (s, 3H, $\text{CH}_3\text{-C=N}$), 1.70 (s, 3H, $\text{CH}_3\text{-C=O}$).

2-(2,6-Dimethylphenyl)imino-3-butanone (1b). A procedure identical to that for **1a** was used, although purification with benzene/pentane was not necessary. (yield 92%). ^1H NMR (C_6D_6 , 25°C) δ = 6.90 (m, 3H, Ph), 2.35 (s, 3H, $\text{CH}_3\text{-C=N}$), 1.75 (s, 6H, Ph-Me), 1.58 (s, 3H, $\text{CH}_3\text{-C=O}$). ^{13}C NMR (C_6D_6 , 25°C) δ = 198.8, 166.8, 147.9, 128.3, 124.0, 123.6.

2-(2,6-Diisopropylphenyl)imino-3-butanone (1c). A procedure identical to that for **1a** was used, although like **1b**, purification with benzene/pentane was not necessary. (yield 92%). ^1H NMR (C_6D_6 , 25°C) δ = 7.18 (m, 3H, Ph), 2.55 (sept, 2H, $\text{CH}(\text{CH}_3)_2$), 2.38 (s, 3H, $\text{CH}_3\text{-C=N}$), 1.65 (s, 3H, $\text{CH}_3\text{-C=O}$), 1.05 (dd, 12H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (C_6D_6 , 25°C) δ = 198.8, 167.2, 145.7, 134.9, 124.9, 123.5.

$\text{Li}(\text{NBu}_3)_2$ [2-(*p*-triphenylborato-2,6-Diisopropylphenyl)imino-3-butanone] (1d). A procedure identical to that for **1a** was used, although purification with benzene/pentane was not necessary. ^1H NMR (C_6D_6 , 25°C) δ = 7.75 (m, 6H, o-BPh₃), 7.55 (m, 2H, o-Ph), 7.10 (t, 6H, m-BPh₃), 6.90 (t, 3H, p-BPh₃), 2.60 (dd, 12H, NBu₃), 2.38 (s, 3H, $\text{CH}_3\text{-C=N}$), 1.78 (s, 3H, $\text{CH}_3\text{-C=O}$), 1.20 (m, 24H, NBu₃), 1.05 (dd, 12H, $\text{CH}(\text{CH}_3)_2$), 0.85 (t, 18H, NBu₃).

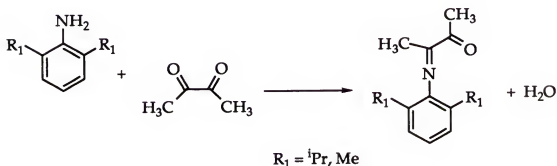
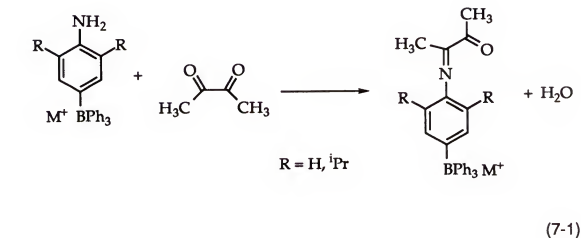
2,3-N,N'-Bis(*p*-bromoaniline)butanediimine (2). To a solution of *p*-bromoaniline (0.50 g, 2.9 mmol) in 10 mL methanol was added a drop of formic acid (88 % solution) followed by butadione (0.13 mL, 1.45 mmol) and the yellow solution stirred at room temperature for 12 hours. The resulting yellow precipitate was filtered and dried *in vacuo* yielding **2** (0.15g, 28%) as a yellow solid. ^1H NMR (C_6D_6 , 25°C) δ = 7.24 (d, 4H, Ph), 6.34 (d, 4H, Ph), 1.92 (s, 6H, CH₃).

Results and Discussion

The synthesis of diimine ligands is typically accomplished using an acid catalyst, such as formic acid, which provides a difficulty in the synthesis of borate-containing diimine ligands. Since the aniline-borate used in this study are highly acid-sensitive, acid catalysis cannot be used. Attempts to use formic acid as a catalyst for the synthesis of borate-containing diimine ligands verified this expectation, and complete decomposition of the borate occurred. Diimine ligands are also prepared using base catalysts, and the synthesis of borate-containing diimines was also attempted using triethylamine as a catalyst. However, this led to a mixture of products that appeared to be the result of some oligomerization process of the butadione. Therefore, other methods for the synthesis of borate-containing diimines must be found.

Although the yields are relatively low (<50%), and the reaction time is long (>1 week) the 2,3-diphenyldiimine ligand can be prepared in MeOH without the presence of a catalyst. However, this does not seem to occur for the more bulky 2,6-dialkylated anilines. The condensation of an aniline with butadione was determined to occur without the presence of any catalyst, and when an aniline is dissolved in 25 equivalents of butadione, an α -ketoimine is formed. This reaction can be accomplished using anilines, or borate-substituted anilines (equation 7-1). It was found that when the reaction was allowed to proceed longer than six hours, oligomerization of the butadione occurred, and additional purification of the keto-imines was required. In the case of the non-borated anilines, this was accomplished by extracting the ketoimine into hexanes. However, in the case of the borate-containing anilines, purification was accomplished by washing the product with benzene. These mono-imines show great promise in the synthesis of borate-containing

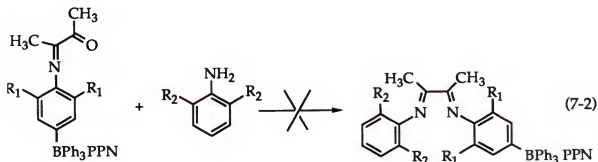
diimines, since they allow for the possibility of preparing diimine ligands containing only one borate group.



The synthesis of the diimine ligand from two equivalents of *p*-bromoaniline was accomplished, and the halo-lithium exchange reaction was examined with this ligand. Thus, in THF at -78°C , BuLi was added, and after 20 minutes at -78°C , BPh₃ was added. The resulting mixture of products could not be separated, and no evidence of a borate was present by ^1H NMR.

The condensation of a second amine with the remaining carbonyl group has proven to be difficult without the presence of a catalyst. The addition (equation 7-2) of excess aniline to the α -ketoimines does not lead to a

diimine, and no reaction is observed. Therefore, other methods for the second condensation must be determined.



Some methods that may alleviate this problem is the heating of the reactions, which may help drive the condensation. The use of PPN salts of the aniline-borates leads to much more stable salts, and these salts may allow for rather strong heating for the reaction to proceed. Another method for driving the condensation might be the use of isolated anilide anions for condensation with the carbonyl. This may avoid the occurrence of the oligomerization processes like those observed with triethylamine and the dione. However, the use of triethylamine may not cause the same reactivity with the keto-imine, and its use as a catalyst should be examined with the keto-imine. Other base catalysts, such as alkoxides, might also prove to be helpful as catalysts, and their reactivity should be examined.

CHAPTER 8

SUMMARY

The synthesis of long-lived, zwitterionic single-site olefin polymerization catalysts has been of great interest in the last 10 years, and we examined a number of methods for the synthesis of such complexes. Our initial studies examined the direct reaction of an anionic Cp group with multiple borane reagents, and we found that this reaction was specific to the type of borane and Cp anion used. When Cp salts of Na, Tl, MgBr, and TMS were used, mixtures of products were isolated. However, when Li salts of Cp anions were used, the reactions gave more pure products. It was also found that different boranes used gave different types of products. When the bulky, perfluorinated triphenylborane was used, monomeric Cp anions were produced. However, when boron trihalides were used, the Cp products underwent Diels-Alder dimerizations, and the resulting dimers could not be cracked without significant decomposition. Ph_2BOMe did not react with the Cp salts.

In order to avoid Diels-Alder dimerizations, we sought other methods for preparing boron-carbon bonds that would not allow dimerization reactions. We chose hydroboration (Chapter 2) as a likely candidate, since the Cp precursor, $\text{LiCpC}(\text{CH}_3)\text{CH}_2$, could be isolated from the reaction of 6,6-dimethylfulvene and LDA, without concern for dimerizations. We chose $\text{Ph}_2\text{BH}\cdot\text{Py}$ as the hydroborating agent since it gave good selectivity and was easy to prepare. Unfortunately, the hydroboration reaction did not lead to

pure products with group 4 metallocenes, so we examined other Cp-anion forming reactions of 6,6-dimethylfulvene.

6,6-Dimethylfulvene undergoes nucleophilic attack by aryllithium compounds leading to anionic Cp salts. In order to prepare a functionalizable Cp ligand, we used *p*-bromophenyllithium as the nucleophile, which reacts with 6,6-dimethylfulvene to give a functionalizable ligand, $\text{LiCpC}(\text{CH}_3)_2\text{PhBr}$. We prepared the model complex, $\text{Cp}^*\text{RuCpC}(\text{CH}_3)_2\text{PhBr}$, as well as the iodo-analogue, in order to examine (Chapter 3) the possibility of halo-lithium exchange with this ligand. The 18 electron ruthenium complex cleanly undergoes the halo-lithium exchange reaction, and a borate-containing ruthenocene was prepared. However, when similar group 4 metal complexes were prepared (Chapter 4), the halo-lithium exchange reaction led to intractable mixtures of products, probably due to the highly electrophilic metal center. Therefore, we determined that, in order to prepare borate containing group 4 complexes, the borate-containing ligand must be prepared prior to coordination to the metal center. Therefore, we examined other methods for accomplishing this.

Our first study in this area examined the possibility of preparing a functionalizable, tetraarylborate that could be used as a nucleophile. The synthesis of *p*-halophenyltriphenylborates appeared to be a step in the right direction (Chapter 5). However, these new tetraphenylborates did not react with BuLi and undergo halo-lithium exchange. This might be due to the excessive charge on the borate, that would destabilize the anionic lithiate that is formed. Therefore, other methods for making a nucleophilic borate was examined. To do this, tin coupling methods were examined, since it is well known that triaryl- and trialkyl-tin lithium complexes react with aryl halides to prepare new aryl-tin complexes. These reactions were examined with the

p-halophenyltriphenylborates, and new tin-containing borates were prepared. The reactivity of these complexes with halophenyl-containing metallocenes was not examined, although it might lead to new borate-containing metallocenes. This chemistry should be continued. The preparation of tin-containing metallocenes was also accomplished, and these new Cp-tin metallocenes are interesting new complexes that require further studies.

Another method for the synthesis of borate-containing ligands that can be coordinated to metals, was examined. This involved the synthesis of borate-containing anilines, which can then be used in the preparation of borate-containing CpSiNR ligands (Chapter 6). We examined the synthesis of a series of borate-containing anilines, including *p*-triphenylboratoaniline, *p*-triphenylborato-2,6-dimethylaniline, and *p*-triphenylborato-2,6-diisopropylaniline. The *p*-triphenylboratoaniline was used to prepare the first borate-containing CpSiNR ligand, and zirconium complexes with this ligand were also prepared. The synthesis of the zirconium dichloride complex with the CpSiNR ligand did not always give pure reaction products, and methods for isolating the pure zirconium dichloride need to be established. The syntheses of ligands from the 2,6-dialkylated aniline borates also needs to be established, and the reactivity of all of these complexes with olefins, once activated, needs to be determined.

The prepared aniline-borates show a great deal of promise in the synthesis of zwitterionic, late-transition metal diimine catalysts. Initial studies (Chapter 7) show the possibility of preparing mono-borate-containing diimine ligands by first preparing α -ketoimines from excess 2,3-butanedione and any aniline, including borate-containing anilines.

APPENDIX
TABLES OF CRYSTALLOGRAPHIC DATA

Table A-1a. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 3-3. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U (eq)
Ru	2547 (1)	841 (1)	7775 (1)	20 (1)
Br	-4164 (1)	1696 (1)	13143 (1)	42 (1)
C (1)	2770 (3)	1177 (1)	5405 (3)	27 (1)
C (1')	1988 (4)	1584 (2)	4358 (4)	40 (1)
C (2)	3917 (3)	1287 (1)	6557 (4)	27 (1)
C (2')	4467 (4)	1832 (2)	7013 (5)	46 (1)
C (3)	4490 (3)	782 (1)	7122 (4)	28 (1)
C (3')	5743 (3)	701 (2)	8266 (5)	44 (1)
C (4')	3974 (4)	-226 (1)	6523 (5)	40 (1)
C (4)	3688 (3)	362 (1)	6338 (4)	27 (1)
C (5)	2621 (3)	603 (1)	5284 (3)	26 (1)
C (5')	1576 (4)	312 (2)	4180 (4)	39 (1)
C (6)	908 (3)	1159 (1)	8898 (3)	22 (1)
C (7)	2119 (3)	1243 (1)	9955 (3)	27 (1)
C (8)	2706 (3)	738 (2)	10380 (4)	34 (1)
C (9)	1875 (3)	334 (1)	9604 (4)	32 (1)
C (10)	764 (3)	588 (1)	8684 (4)	26 (1)
C (11)	-124 (3)	1578 (1)	8358 (3)	25 (1)
C (12)	520 (4)	2125 (1)	8174 (5)	41 (1)
C (13)	-941 (3)	1416 (2)	6723 (4)	38 (1)
C (14)	-1053 (3)	1621 (1)	9624 (3)	23 (1)
C (15)	-1001 (3)	1271 (1)	10925 (4)	28 (1)
C (16)	-1891 (3)	1299 (1)	12004 (4)	30 (1)
C (17)	-2862 (3)	1685 (1)	11769 (4)	28 (1)
C (18)	-2921 (3)	2051 (1)	10532 (4)	32 (1)
C (19)	-2025 (3)	2018 (1)	9467 (4)	30 (1)

Table A-1b. Bond lengths [Å] and angles [deg] for 3-3.

Ru-C(3)	2.171(3)
Ru-C(4)	2.173(3)
Ru-C(2)	2.178(3)
Ru-C(8)	2.178(3)
Ru-C(5)	2.182(3)
Ru-C(9)	2.185(3)
Ru-C(7)	2.189(3)
Ru-C(10)	2.198(3)
Ru-C(1)	2.199(3)
Ru-C(6)	2.213(3)
Br-C(17)	1.906(3)
C(1)-C(2)	1.435(4)
C(1)-C(5)	1.442(4)
C(1)-C(1')	1.495(4)
C(2)-C(3)	1.441(4)
C(2)-C(2')	1.500(4)
C(3)-C(4)	1.431(4)
C(3)-C(3')	1.501(4)
C(4')-C(4)	1.501(4)
C(4)-C(5)	1.433(4)
C(5)-C(5')	1.496(4)
C(6)-C(7)	1.433(4)
C(6)-C(10)	1.440(4)
C(6)-C(11)	1.513(4)
C(7)-C(8)	1.421(5)
C(8)-C(9)	1.416(5)
C(9)-C(10)	1.429(4)
C(11)-C(12)	1.536(4)
C(11)-C(14)	1.543(4)
C(11)-C(13)	1.548(4)
C(14)-C(15)	1.391(4)
C(14)-C(19)	1.405(4)
C(15)-C(16)	1.390(4)
C(16)-C(17)	1.385(4)
C(17)-C(18)	1.375(5)
C(18)-C(19)	1.387(4)
C(3)-Ru-C(4)	38.46(11)
C(3)-Ru-C(2)	38.69(12)
C(4)-Ru-C(2)	64.57(11)
C(3)-Ru-C(8)	108.47(12)
C(4)-Ru-C(8)	121.84(12)
C(2)-Ru-C(8)	125.27(12)
C(3)-Ru-C(5)	64.38(11)
C(4)-Ru-C(5)	38.41(12)
C(2)-Ru-C(5)	64.44(11)
C(8)-Ru-C(5)	156.47(13)
C(3)-Ru-C(9)	123.15(12)
C(4)-Ru-C(9)	109.29(11)
C(2)-Ru-C(9)	158.01(12)
C(8)-Ru-C(9)	37.88(13)
C(5)-Ru-C(9)	125.09(12)
C(3)-Ru-C(7)	123.96(11)
C(4)-Ru-C(7)	155.97(12)
C(2)-Ru-C(7)	112.91(11)

C(8)-Ru-C(7)	37.98(12)
C(5)-Ru-C(7)	164.73(12)
C(9)-Ru-C(7)	63.37(12)
C(3)-Ru-C(10)	158.39(12)
C(4)-Ru-C(10)	126.39(11)
C(2)-Ru-C(10)	162.46(12)
C(8)-Ru-C(10)	63.53(12)
C(5)-Ru-C(10)	114.21(11)
C(9)-Ru-C(10)	38.06(11)
C(7)-Ru-C(10)	63.33(11)
C(3)-Ru-C(1)	64.28(11)
C(4)-Ru-C(1)	64.27(11)
C(2)-Ru-C(1)	38.26(11)
C(8)-Ru-C(1)	161.33(13)
C(5)-Ru-C(1)	38.43(11)
C(9)-Ru-C(1)	160.69(13)
C(7)-Ru-C(1)	130.00(12)
C(10)-Ru-C(1)	129.42(11)
C(3)-Ru-C(6)	159.19(11)
C(4)-Ru-C(6)	162.30(11)
C(2)-Ru-C(6)	128.05(11)
C(8)-Ru-C(6)	63.83(11)
C(5)-Ru-C(6)	130.43(11)
C(9)-Ru-C(6)	63.83(11)
C(7)-Ru-C(6)	37.99(10)
C(10)-Ru-C(6)	38.10(10)
C(1)-Ru-C(6)	116.36(11)
C(2)-C(1)-C(5)	107.8(3)
C(2)-C(1)-C(1')	125.4(3)
C(5)-C(1)-C(1')	126.3(3)
C(2)-C(1)-Ru	70.1(2)
C(5)-C(1)-Ru	70.2(2)
C(1')-C(1)-Ru	131.6(2)
C(1)-C(2)-C(3)	107.9(3)
C(1)-C(2)-C(2')	125.9(3)
C(3)-C(2)-C(2')	126.1(3)
C(1)-C(2)-Ru	71.7(2)
C(3)-C(2)-Ru	70.4(2)
C(2')-C(2)-Ru	126.3(2)
C(4)-C(3)-C(2)	108.1(3)
C(4)-C(3)-C(3')	125.2(3)
C(2)-C(3)-C(3')	126.7(3)
C(4)-C(3)-Ru	70.8(2)
C(2)-C(3)-Ru	70.9(2)
C(3')-C(3)-Ru	126.3(2)
C(3)-C(4)-C(5)	108.2(3)
C(3)-C(4)-C(4')	125.2(3)
C(5)-C(4)-C(4')	126.4(3)
C(3)-C(4)-Ru	70.7(2)
C(5)-C(4)-Ru	71.2(2)
C(4')-C(4)-Ru	126.6(2)
C(4)-C(5)-C(1)	108.0(3)
C(4)-C(5)-C(5')	126.3(3)
C(1)-C(5)-C(5')	125.7(3)
C(4)-C(5)-Ru	70.4(2)
C(1)-C(5)-Ru	71.4(2)
C(5')-C(5)-Ru	126.3(2)
C(7)-C(6)-C(10)	106.6(3)

C(7)-C(6)-C(11)	126.3(3)
C(10)-C(6)-C(11)	126.3(3)
C(7)-C(6)-Ru	70.1(2)
C(10)-C(6)-Ru	70.4(2)
C(11)-C(6)-Ru	132.3(2)
C(8)-C(7)-C(6)	108.9(3)
C(8)-C(7)-Ru	70.6(2)
C(6)-C(7)-Ru	71.9(2)
C(9)-C(8)-C(7)	108.1(3)
C(9)-C(8)-Ru	71.3(2)
C(7)-C(8)-Ru	71.4(2)
C(8)-C(9)-C(10)	108.1(3)
C(8)-C(9)-Ru	70.8(2)
C(10)-C(9)-Ru	71.5(2)
C(9)-C(10)-C(6)	108.3(3)
C(9)-C(10)-Ru	70.5(2)
C(6)-C(10)-Ru	71.5(2)
C(6)-C(11)-C(12)	110.3(3)
C(6)-C(11)-C(14)	109.3(2)
C(12)-C(11)-C(14)	109.6(2)
C(6)-C(11)-C(13)	110.2(2)
C(12)-C(11)-C(13)	109.2(3)
C(14)-C(11)-C(13)	108.2(2)
C(15)-C(14)-C(19)	117.1(3)
C(15)-C(14)-C(11)	122.9(3)
C(19)-C(14)-C(11)	120.0(3)
C(16)-C(15)-C(14)	121.9(3)
C(17)-C(16)-C(15)	118.9(3)
C(18)-C(17)-C(16)	121.0(3)
C(18)-C(17)-Br	119.6(2)
C(16)-C(17)-Br	119.4(2)
C(17)-C(18)-C(19)	119.4(3)
C(18)-C(19)-C(14)	121.6(3)

Symmetry transformations used to generate equivalent atoms:

Table A-1c. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 3-3.
 The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Ru	20(1)	24(1)	16(1)	0(1)	5(1)	0(1)
Br	42(1)	40(1)	51(1)	-9(1)	26(1)	3(1)
C(1)	34(2)	32(2)	17(1)	4(1)	11(1)	1(1)
C(1')	54(2)	42(2)	26(2)	12(1)	13(2)	13(2)
C(2)	32(2)	30(2)	24(1)	0(1)	14(1)	-6(1)
C(2')	54(2)	36(2)	50(2)	-7(2)	20(2)	-17(2)
C(3)	21(1)	36(2)	28(2)	-1(1)	13(1)	0(1)
C(3')	24(2)	61(2)	47(2)	2(2)	6(1)	2(2)
C(4')	51(2)	30(2)	43(2)	2(1)	25(2)	4(2)
C(4)	30(1)	28(2)	28(2)	1(1)	17(1)	2(1)
C(5)	33(2)	31(2)	17(1)	-4(1)	12(1)	-5(1)
C(5')	44(2)	52(2)	23(2)	-11(1)	9(1)	-16(2)
C(6)	23(1)	27(1)	18(1)	-3(1)	7(1)	0(1)
C(7)	24(1)	39(2)	18(1)	-7(1)	6(1)	-1(1)
C(8)	31(2)	55(2)	16(1)	6(1)	7(1)	12(1)
C(9)	39(2)	34(2)	27(2)	12(1)	20(1)	8(1)
C(10)	24(1)	28(1)	28(1)	0(1)	10(1)	-3(1)
C(11)	26(1)	27(1)	22(1)	1(1)	6(1)	2(1)
C(12)	42(2)	28(2)	56(2)	6(2)	21(2)	1(1)
C(13)	35(2)	57(2)	21(2)	1(1)	4(1)	13(2)
C(14)	23(1)	24(1)	23(1)	-3(1)	3(1)	1(1)
C(15)	26(1)	31(2)	28(2)	1(1)	6(1)	6(1)
C(16)	30(2)	32(2)	29(2)	2(1)	10(1)	3(1)
C(17)	27(1)	31(2)	29(2)	-9(1)	10(1)	-1(1)
C(18)	31(2)	29(2)	36(2)	-5(1)	8(1)	9(1)
C(19)	33(2)	28(2)	30(2)	1(1)	8(1)	7(1)

Table A-1d. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 3-3.

	x	y	z	U (eq)
H (1'A)	1269 (4)	1410 (2)	3693 (4)	60
H (1'B)	2533 (4)	1755 (2)	3684 (4)	60
H (1'C)	1658 (4)	1847 (2)	5026 (4)	60
H (2'A)	5237 (4)	1796 (2)	7808 (5)	68
H (2'B)	3827 (4)	2041 (2)	7451 (5)	68
H (2'C)	4687 (4)	2007 (2)	6071 (5)	68
H (3'A)	6098 (3)	1043 (2)	8630 (5)	66
H (3'B)	6357 (3)	514 (2)	7721 (5)	66
H (3'C)	5575 (3)	494 (2)	9177 (5)	66
H (4'A)	3292 (4)	-426 (1)	5876 (5)	60
H (4'B)	4019 (4)	-326 (1)	7638 (5)	60
H (4'C)	4794 (4)	-303 (1)	6175 (5)	60
H (5'A)	981 (4)	568 (2)	3608 (4)	59
H (5'B)	1110 (4)	80 (2)	4803 (4)	59
H (5'C)	1967 (4)	104 (2)	3419 (4)	59
H (7A)	2466 (3)	1592 (1)	10357 (3)	32
H (8A)	3517 (3)	678 (2)	11134 (4)	40
H (9A)	2013 (3)	-54 (1)	9724 (4)	38
H (10A)	15 (3)	405 (1)	8054 (4)	31
H (12A)	-144 (4)	2387 (1)	7831 (5)	61
H (12B)	1094 (4)	2098 (1)	7382 (5)	61
H (12C)	1012 (4)	2231 (1)	9192 (5)	61
H (13A)	-1592 (3)	1684 (2)	6393 (4)	57
H (13B)	-1361 (3)	1078 (2)	6840 (4)	57
H (13C)	-378 (3)	1383 (2)	5921 (4)	57
H (15A)	-351 (3)	1010 (1)	11078 (4)	34
H (16A)	-1836 (3)	1062 (1)	12869 (4)	36
H (18A)	-3556 (3)	2318 (1)	10411 (4)	38
H (19A)	-2069 (3)	2265 (1)	8629 (4)	36

Table A-2a. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3-6b**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Ru	275(1)	2201(1)	118(1)	26(1)
B	1601(1)	-2204(2)	-1621(2)	25(1)
C(1)	171(1)	3656(2)	-47(2)	40(1)
C(1')	414(1)	4401(2)	-252(3)	57(1)
C(2)	86(1)	3393(2)	711(2)	36(1)
C(2')	221(1)	3799(3)	1435(2)	58(1)
C(3)	-168(1)	2714(2)	670(2)	31(1)
C(3')	-347(1)	2303(3)	1339(2)	44(1)
C(4)	-238(1)	2547(2)	-117(2)	32(1)
C(4')	-503(1)	1932(2)	-423(2)	40(1)
C(5)	-30(1)	3139(2)	-557(2)	35(1)
C(5')	-50(1)	3269(3)	-1404(2)	50(1)
C(6)	776(1)	1846(2)	-202(2)	36(1)
C(7)	749(1)	1842(2)	605(2)	42(1)
C(8)	519(1)	1148(2)	807(2)	37(1)
C(9)	408(1)	724(2)	129(2)	28(1)
C(10)	566(1)	1149(2)	-504(2)	26(1)
C(11)	632(1)	1583(2)	-1874(2)	48(1)
C(12)	224(1)	373(3)	-1495(2)	42(1)
C(13)	561(1)	789(2)	-1317(2)	29(1)
C(14)	825(1)	37(2)	-1405(2)	25(1)
C(15)	876(1)	-415(2)	-2099(2)	30(1)
C(16)	1110(1)	-1101(2)	-2183(2)	29(1)
C(17)	1313(1)	-1399(2)	-1593(2)	24(1)
C(18)	1260(1)	-929(2)	-908(2)	30(1)
C(19)	1026(1)	-248(2)	-813(2)	29(1)
C(20)	1662(1)	-2602(2)	-2484(2)	29(1)
C(21)	1403(1)	-3001(2)	-2888(2)	35(1)
C(22)	1438(1)	-3361(3)	-3616(2)	49(1)
C(23)	1737(1)	-3349(3)	-3962(2)	62(1)
C(24)	2000(1)	-2991(3)	-3582(2)	66(1)
C(25)	1963(1)	-2620(3)	-2847(2)	44(1)
C(26)	1927(1)	-1693(2)	-1270(2)	30(1)
C(27)	2050(1)	-1864(3)	-544(2)	49(1)
C(28)	2303(1)	-1333(4)	-234(3)	66(1)
C(29)	2448(1)	-647(3)	-633(3)	68(1)
C(30)	2337(1)	-460(3)	-1345(3)	62(1)
C(31)	2082(1)	-968(2)	-1653(2)	45(1)
C(32)	1497(1)	-3098(2)	-1100(2)	28(1)
C(33)	1705(1)	-3865(2)	-1039(2)	40(1)
C(34)	1626(1)	-4640(3)	-611(2)	49(1)
C(35)	1334(1)	-4686(3)	-228(2)	51(1)
C(36)	1121(1)	-3958(3)	-280(2)	45(1)
C(37)	1202(1)	-3180(2)	-708(2)	35(1)
Li	1621(2)	7363(4)	2424(4)	46(1)
O(40)	1215(1)	6740(2)	2550(1)	52(1)
C(41)	1031(6)	6359(14)	1927(8)	91(7)
C(42)	874(5)	5491(12)	2212(14)	99(9)
C(43)	1072(4)	5224(10)	2890(9)	61(4)

C (44)	1172 (5)	6146 (8)	3199 (5)	56 (3)
C (41')	1029 (4)	6545 (10)	1875 (6)	56 (3)
C (42')	983 (4)	5518 (10)	1894 (7)	76 (4)
C (43')	924 (6)	5320 (11)	2715 (9)	85 (7)
C (44')	1126 (6)	6046 (11)	3098 (8)	94 (7)
O (50)	1593 (1)	8468 (2)	1820 (2)	64 (1)
C (51)	1882 (2)	9027 (7)	1660 (7)	60 (3)
C (52)	1787 (3)	9849 (12)	1211 (13)	118 (9)
C (53)	1427 (3)	9897 (10)	1170 (12)	52 (4)
C (54)	1343 (3)	8932 (9)	1374 (11)	52 (5)
C (51')	1722 (3)	9317 (3)	2152 (5)	62 (3)
C (52')	1696 (3)	9991 (6)	1524 (5)	54 (3)
C (53')	1403 (3)	9650 (8)	1119 (9)	61 (4)
C (54')	1339 (3)	8658 (8)	1264 (8)	57 (3)
O (60)	1905 (1)	6498 (2)	1930 (1)	58 (1)
C (61)	2150 (5)	6921 (10)	1468 (16)	108 (10)
C (62)	2357 (5)	6194 (12)	1130 (15)	112 (10)
C (63)	2256 (5)	5319 (14)	1493 (18)	105 (13)
C (64)	1958 (6)	5522 (4)	1935 (24)	161 (18)
C (61')	2000 (3)	6518 (9)	1151 (3)	116 (5)
C (62')	2238 (2)	5763 (9)	1031 (4)	92 (4)
C (63')	2310 (3)	5413 (8)	1800 (5)	80 (3)
C (64')	2009 (2)	5628 (4)	2227 (5)	69 (3)
O (70)	1793 (1)	7737 (2)	3388 (2)	60 (1)
C (71)	1618 (2)	8515 (8)	3705 (8)	80 (4)
C (72)	1823 (4)	8625 (19)	4414 (11)	72 (4)
C (73)	2157 (6)	8174 (17)	4429 (10)	64 (4)
C (74)	2094 (3)	7512 (11)	3779 (9)	107 (7)
C (71')	1607 (2)	8029 (8)	4044 (4)	50 (2)
C (72')	1804 (4)	8685 (16)	4536 (11)	72 (4)
C (73')	2108 (5)	8113 (17)	4398 (8)	67 (4)
C (74')	2136 (1)	7825 (7)	3574 (5)	34 (2)

Table A-2b. Bond lengths [Å] and angles [deg] for 3-6b.

Ru-C(2)	2.159(3)
Ru-C(1)	2.164(3)
Ru-C(7)	2.182(3)
Ru-C(6)	2.185(3)
Ru-C(8)	2.186(3)
Ru-C(3)	2.189(3)
Ru-C(5)	2.195(3)
Ru-C(4)	2.197(3)
Ru-C(9)	2.201(3)
Ru-C(10)	2.220(3)
B-C(32)	1.641(5)
B-C(20)	1.645(4)
B-C(26)	1.648(5)
B-C(17)	1.654(4)
C(1)-C(2)	1.432(5)
C(1)-C(5)	1.430(5)
C(1)-C(1')	1.510(5)
C(2)-C(3)	1.430(5)
C(2)-C(2')	1.511(5)
C(3)-C(4)	1.437(5)
C(3)-C(3')	1.510(5)
C(4)-C(5)	1.432(5)
C(4)-C(4')	1.501(5)
C(5)-C(5')	1.508(5)
C(6)-C(7)	1.427(5)
C(6)-C(10)	1.427(4)
C(7)-C(8)	1.422(5)
C(8)-C(9)	1.418(4)
C(9)-C(10)	1.429(4)
C(10)-C(13)	1.525(4)
C(11)-C(13)	1.537(4)
C(12)-C(13)	1.537(4)
C(13)-C(14)	1.539(4)
C(14)-C(19)	1.391(4)
C(14)-C(15)	1.403(4)
C(15)-C(16)	1.385(4)
C(16)-C(17)	1.399(4)
C(17)-C(18)	1.404(4)
C(18)-C(19)	1.382(4)
C(20)-C(25)	1.389(5)
C(20)-C(21)	1.402(5)
C(21)-C(22)	1.391(5)
C(22)-C(23)	1.370(6)
C(23)-C(24)	1.369(6)
C(24)-C(25)	1.410(5)
C(26)-C(27)	1.397(5)
C(26)-C(31)	1.398(5)
C(27)-C(28)	1.398(6)
C(28)-C(29)	1.353(7)
C(29)-C(30)	1.362(7)
C(30)-C(31)	1.388(5)
C(32)-C(37)	1.396(4)
C(32)-C(33)	1.400(4)
C(33)-C(34)	1.387(5)
C(34)-C(35)	1.376(5)

C(35)-C(36)	1.368(5)
C(36)-C(37)	1.392(5)
Li-O(40)	1.903(7)
Li-O(70)	1.918(6)
Li-O(60)	1.916(7)
Li-O(50)	1.921(7)
O(40)-C(44')	1.440(4)
O(40)-C(44)	1.440(4)
O(40)-C(41)	1.440(4)
O(40)-C(41')	1.440(4)
C(41)-C(42)	1.495(5)
C(42)-C(43)	1.495(5)
C(43)-C(44)	1.495(5)
C(41')-C(42')	1.495(5)
C(42')-C(43')	1.495(5)
C(43')-C(44')	1.495(5)
O(50)-C(54)	1.457(4)
O(50)-C(54')	1.457(4)
O(50)-C(51)	1.458(4)
O(50)-C(51')	1.458(4)
C(51)-C(52)	1.479(4)
C(52)-C(53)	1.479(4)
C(53)-C(54)	1.479(4)
C(51')-C(52')	1.479(4)
C(52')-C(53')	1.479(4)
C(53')-C(54')	1.479(4)
O(60)-C(64)	1.427(4)
O(60)-C(61')	1.427(4)
O(60)-C(61)	1.427(4)
O(60)-C(64')	1.427(4)
C(61)-C(62)	1.476(5)
C(62)-C(63)	1.476(5)
C(63)-C(64)	1.476(5)
C(61')-C(62')	1.476(5)
C(62')-C(63')	1.476(5)
C(63')-C(64')	1.476(5)
O(70)-C(74)	1.446(4)
O(70)-C(74')	1.447(4)
O(70)-C(71')	1.447(4)
O(70)-C(71)	1.447(4)
C(71)-C(72)	1.515(6)
C(72)-C(73)	1.515(6)
C(73)-C(74)	1.515(6)
C(71')-C(72')	1.515(6)
C(72')-C(73')	1.515(6)
C(73')-C(74')	1.515(6)
C(2)-Ru-C(1)	38.67(13)
C(2)-Ru-C(7)	108.58(13)
C(1)-Ru-C(7)	117.36(13)
C(2)-Ru-C(6)	130.48(12)
C(1)-Ru-C(6)	112.25(12)
C(7)-Ru-C(6)	38.14(13)
C(2)-Ru-C(8)	116.72(13)
C(1)-Ru-C(8)	147.17(13)
C(7)-Ru-C(8)	37.98(13)
C(6)-Ru-C(8)	63.50(13)
C(2)-Ru-C(3)	38.39(12)

C(1)-Ru-C(3)	64.31(12)
C(7)-Ru-C(3)	129.93(13)
C(6)-Ru-C(3)	166.24(12)
C(8)-Ru-C(3)	111.46(13)
C(2)-Ru-C(5)	64.23(13)
C(1)-Ru-C(5)	38.29(13)
C(7)-Ru-C(5)	150.05(14)
C(6)-Ru-C(5)	122.62(13)
C(8)-Ru-C(5)	171.97(13)
C(3)-Ru-C(5)	63.86(12)
C(2)-Ru-C(4)	64.29(12)
C(1)-Ru-C(4)	64.19(12)
C(7)-Ru-C(4)	167.60(13)
C(6)-Ru-C(4)	154.16(13)
C(8)-Ru-C(4)	134.25(13)
C(3)-Ru-C(4)	38.25(12)
C(5)-Ru-C(4)	38.07(12)
C(2)-Ru-C(9)	149.02(12)
C(1)-Ru-C(9)	172.29(12)
C(7)-Ru-C(9)	63.12(12)
C(6)-Ru-C(9)	62.90(12)
C(8)-Ru-C(9)	37.72(12)
C(3)-Ru-C(9)	121.89(12)
C(5)-Ru-C(9)	137.98(12)
C(4)-Ru-C(9)	117.18(11)
C(2)-Ru-C(10)	167.97(12)
C(1)-Ru-C(10)	134.79(12)
C(7)-Ru-C(10)	63.63(12)
C(6)-Ru-C(10)	37.78(11)
C(8)-Ru-C(10)	63.54(11)
C(3)-Ru-C(10)	153.64(11)
C(5)-Ru-C(10)	117.39(11)
C(4)-Ru-C(10)	125.06(11)
C(9)-Ru-C(10)	37.72(11)
C(32)-B-C(20)	106.4(2)
C(32)-B-C(26)	110.6(2)
C(20)-B-C(26)	112.3(3)
C(32)-B-C(17)	110.6(2)
C(20)-B-C(17)	112.5(2)
C(26)-B-C(17)	104.5(2)
C(2)-C(1)-C(5)	108.0(3)
C(2)-C(1)-C(1')	124.9(3)
C(5)-C(1)-C(1')	126.9(3)
C(2)-C(1)-Ru	70.5(2)
C(5)-C(1)-Ru	72.0(2)
C(1')-C(1)-Ru	126.4(2)
C(3)-C(2)-C(1)	108.2(3)
C(3)-C(2)-C(2')	125.1(3)
C(1)-C(2)-C(2')	126.6(3)
C(3)-C(2)-Ru	72.0(2)
C(1)-C(2)-Ru	70.9(2)
C(2')-C(2)-Ru	125.9(2)
C(2)-C(3)-C(4)	107.9(3)
C(2)-C(3)-C(3')	125.6(3)
C(4)-C(3)-C(3')	126.3(3)
C(2)-C(3)-Ru	69.6(2)
C(4)-C(3)-Ru	71.2(2)
C(3')-C(3)-Ru	128.0(2)

C (5) -C (4) -C (3)	107.8 (3)
C (5) -C (4) -C (4')	125.8 (3)
C (3) -C (4) -C (4')	126.1 (3)
C (5) -C (4) -Ru	70.9 (2)
C (3) -C (4) -Ru	70.6 (2)
C (4') -C (4) -Ru	128.6 (2)
C (4) -C (5) -C (1)	108.1 (3)
C (4) -C (5) -C (5')	125.5 (3)
C (1) -C (5) -C (5')	126.0 (3)
C (4) -C (5) -Ru	71.1 (2)
C (1) -C (5) -Ru	69.7 (2)
C (5') -C (5) -Ru	130.2 (2)
C (7) -C (6) -C (10)	108.8 (3)
C (7) -C (6) -Ru	70.8 (2)
C (10) -C (6) -Ru	72.4 (2)
C (8) -C (7) -C (6)	107.7 (3)
C (8) -C (7) -Ru	71.2 (2)
C (6) -C (7) -Ru	71.0 (2)
C (9) -C (8) -C (7)	107.8 (3)
C (9) -C (8) -Ru	71.7 (2)
C (7) -C (8) -Ru	70.9 (2)
C (8) -C (9) -C (10)	109.1 (3)
C (8) -C (9) -Ru	70.6 (2)
C (10) -C (9) -Ru	71.9 (2)
C (6) -C (10) -C (9)	106.5 (3)
C (6) -C (10) -C (13)	126.8 (3)
C (9) -C (10) -C (13)	125.6 (3)
C (6) -C (10) -Ru	69.8 (2)
C (9) -C (10) -Ru	70.4 (2)
C (13) -C (10) -Ru	133.7 (2)
C (10) -C (13) -C (12)	109.6 (3)
C (10) -C (13) -C (11)	110.1 (3)
C (12) -C (13) -C (11)	109.4 (3)
C (10) -C (13) -C (14)	109.0 (2)
C (12) -C (13) -C (14)	109.5 (3)
C (11) -C (13) -C (14)	109.2 (3)
C (19) -C (14) -C (15)	115.5 (3)
C (19) -C (14) -C (13)	123.2 (3)
C (15) -C (14) -C (13)	121.3 (3)
C (16) -C (15) -C (14)	121.9 (3)
C (15) -C (16) -C (17)	123.5 (3)
C (16) -C (17) -C (18)	113.4 (3)
C (16) -C (17) -B	128.1 (3)
C (18) -C (17) -B	118.5 (2)
C (19) -C (18) -C (17)	123.9 (3)
C (18) -C (19) -C (14)	121.9 (3)
C (25) -C (20) -C (21)	115.3 (3)
C (25) -C (20) -B	124.7 (3)
C (21) -C (20) -B	119.9 (3)
C (22) -C (21) -C (20)	123.1 (3)
C (23) -C (22) -C (21)	119.9 (4)
C (24) -C (23) -C (22)	119.3 (3)
C (23) -C (24) -C (25)	120.7 (4)
C (20) -C (25) -C (24)	121.7 (4)
C (27) -C (26) -C (31)	114.4 (3)
C (27) -C (26) -B	123.9 (3)
C (31) -C (26) -B	121.4 (3)
C (28) -C (27) -C (26)	121.8 (4)

C(29)-C(28)-C(27)	121.6(4)
C(28)-C(29)-C(30)	118.5(4)
C(29)-C(30)-C(31)	120.5(4)
C(30)-C(31)-C(26)	123.2(4)
C(37)-C(32)-C(33)	114.8(3)
C(37)-C(32)-B	124.6(3)
C(33)-C(32)-B	120.6(3)
C(34)-C(33)-C(32)	122.7(3)
C(35)-C(34)-C(33)	120.5(3)
C(36)-C(35)-C(34)	118.8(3)
C(35)-C(36)-C(37)	120.4(3)
C(36)-C(37)-C(32)	122.8(3)
O(40)-Li-O(70)	110.5(3)
O(40)-Li-O(60)	105.9(3)
O(70)-Li-O(60)	111.3(3)
O(40)-Li-O(50)	114.0(3)
O(70)-Li-O(50)	106.2(3)
O(60)-Li-O(50)	109.0(3)
C(44)-O(40)-C(41)	108.3(9)
C(44')-O(40)-C(41')	106.5(10)
C(44')-O(40)-Li	129.0(10)
C(44)-O(40)-Li	118.7(8)
C(41)-O(40)-Li	123.2(9)
C(41')-O(40)-Li	117.2(7)
O(40)-C(41)-C(42)	106.7(9)
C(43)-C(42)-C(41)	104.6(11)
C(42)-C(43)-C(44)	102.1(13)
O(40)-C(44)-C(43)	106.0(9)
O(40)-C(41')-C(42')	104.0(9)
C(41')-C(42')-C(43')	103.4(11)
C(44')-C(43')-C(42')	102.4(11)
O(40)-C(44')-C(43')	108.9(9)
C(54)-O(50)-C(51)	102.2(8)
C(54')-O(50)-C(51')	111.7(6)
C(54)-O(50)-Li	136.3(7)
C(54')-O(50)-Li	124.9(6)
C(51)-O(50)-Li	121.3(4)
C(51')-O(50)-Li	117.1(3)
O(50)-C(51)-C(52)	109.6(8)
C(53)-C(52)-C(51)	109.0(11)
C(52)-C(53)-C(54)	100.1(12)
O(50)-C(54)-C(53)	113.7(10)
O(50)-C(51')-C(52')	103.1(6)
C(51')-C(52')-C(53')	101.6(8)
C(52')-C(53')-C(54')	112.6(9)
O(50)-C(54')-C(53')	99.9(8)
C(64)-O(60)-C(61)	108.6(10)
C(61')-O(60)-C(64')	106.8(5)
C(64)-O(60)-Li	137.3(9)
C(61')-O(60)-Li	126.2(4)
C(61)-O(60)-Li	114.0(7)
C(64')-O(60)-Li	126.0(4)
O(60)-C(61)-C(62)	109.3(11)
C(61)-C(62)-C(63)	105.8(14)
C(64)-C(63)-C(62)	107(2)
O(60)-C(64)-C(63)	108.6(13)
O(60)-C(61')-C(62')	107.6(5)
C(61')-C(62')-C(63')	104.7(7)

C(62')-C(63')-C(64')	103.3(7)
O(60)-C(64')-C(63')	104.3(6)
C(74')-O(70)-C(71')	107.7(6)
C(74)-O(70)-C(71)	114.4(7)
C(74)-O(70)-Li	132.2(7)
C(74')-O(70)-Li	125.6(5)
C(71')-O(70)-Li	126.6(4)
C(71)-O(70)-Li	112.1(5)
O(70)-C(71)-C(72)	97.1(10)
C(71)-C(72)-C(73)	118.1(13)
C(74)-C(73)-C(72)	96(2)
O(70)-C(74)-C(73)	111.4(10)
O(70)-C(71')-C(72')	111.2(9)
C(73')-C(72')-C(71')	90.1(14)
C(72')-C(73')-C(74')	111.5(12)
O(70)-C(74')-C(73')	99.6(9)

Symmetry transformations used to generate equivalent atoms:

Table A-2c. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 3-6b.
 The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Ru	24(1)	23(1)	32(1)	-4(1)	-1(1)	2(1)
B	27(2)	27(2)	20(2)	0(1)	2(1)	5(2)
C(1)	32(2)	22(2)	64(2)	-3(2)	11(2)	2(1)
C(1')	51(2)	30(2)	89(3)	2(2)	19(2)	-4(2)
C(2)	32(2)	27(2)	49(2)	-11(2)	3(2)	4(1)
C(2')	59(3)	48(2)	66(3)	-28(2)	-2(2)	2(2)
C(3)	24(2)	29(2)	41(2)	-4(1)	5(1)	5(1)
C(3')	42(2)	49(2)	42(2)	1(2)	10(2)	4(2)
C(4)	27(2)	27(2)	41(2)	1(1)	2(1)	7(1)
C(4')	27(2)	42(2)	50(2)	-1(2)	-5(2)	3(2)
C(5)	31(2)	30(2)	44(2)	5(2)	6(2)	12(1)
C(5')	51(2)	54(2)	45(2)	15(2)	6(2)	21(2)
C(6)	24(2)	31(2)	52(2)	-7(2)	0(2)	1(1)
C(7)	30(2)	44(2)	52(2)	-19(2)	-15(2)	11(2)
C(8)	38(2)	39(2)	33(2)	-2(2)	-8(2)	14(2)
C(9)	25(2)	27(2)	32(2)	0(1)	-3(1)	6(1)
C(10)	23(2)	24(2)	30(2)	-2(1)	-2(1)	6(1)
C(11)	65(3)	39(2)	41(2)	11(2)	7(2)	22(2)
C(12)	32(2)	56(2)	38(2)	-13(2)	-10(2)	10(2)
C(13)	31(2)	30(2)	26(2)	1(1)	0(1)	6(1)
C(14)	25(2)	23(2)	27(2)	1(1)	-1(1)	0(1)
C(15)	36(2)	33(2)	21(2)	0(1)	-6(1)	5(1)
C(16)	35(2)	33(2)	18(2)	-2(1)	1(1)	3(1)
C(17)	29(2)	21(2)	23(2)	2(1)	1(1)	1(1)
C(18)	34(2)	34(2)	22(2)	-2(1)	-5(1)	9(1)
C(19)	33(2)	33(2)	21(2)	-5(1)	-1(1)	5(1)
C(20)	43(2)	22(2)	24(2)	2(1)	3(1)	7(1)
C(21)	44(2)	29(2)	33(2)	-4(1)	-2(2)	5(2)
C(22)	74(3)	39(2)	34(2)	-11(2)	-13(2)	9(2)
C(23)	98(4)	61(3)	27(2)	-13(2)	6(2)	13(3)
C(24)	78(3)	77(3)	42(2)	-9(2)	31(2)	11(3)
C(25)	52(2)	47(2)	34(2)	-7(2)	11(2)	3(2)
C(26)	27(2)	33(2)	32(2)	-8(1)	2(1)	8(1)
C(27)	40(2)	69(3)	37(2)	-4(2)	-5(2)	0(2)
C(28)	52(3)	93(4)	54(3)	-19(3)	-21(2)	2(3)
C(29)	35(2)	71(3)	97(4)	-38(3)	-8(2)	0(2)
C(30)	43(2)	46(2)	97(4)	-16(2)	9(2)	-8(2)
C(31)	41(2)	37(2)	56(2)	-4(2)	-1(2)	-2(2)
C(32)	32(2)	32(2)	22(2)	-2(1)	0(1)	2(1)
C(33)	38(2)	40(2)	42(2)	11(2)	4(2)	9(2)
C(34)	57(2)	38(2)	51(2)	13(2)	-4(2)	12(2)
C(35)	64(3)	42(2)	48(2)	20(2)	2(2)	-3(2)
C(36)	47(2)	48(2)	42(2)	10(2)	11(2)	-5(2)
C(37)	37(2)	33(2)	35(2)	4(1)	2(2)	2(2)
Li	45(3)	48(3)	44(3)	-5(2)	-10(2)	1(2)
O(40)	51(2)	56(2)	50(2)	1(1)	-5(1)	-7(1)
C(41)	96(13)	90(14)	86(10)	15(8)	-45(10)	-42(10)
C(42)	77(13)	66(8)	154(21)	27(10)	-61(16)	-28(8)
C(43)	61(9)	49(6)	71(7)	-9(5)	-6(6)	-9(6)

C(44)	69(8)	33(6)	65(7)	-2(4)	9(6)	6(5)
C(41')	49(7)	51(6)	69(7)	-7(5)	-14(6)	-7(5)
C(42')	84(10)	63(7)	81(7)	-17(6)	16(7)	-26(6)
C(43')	106(19)	55(7)	95(12)	-4(7)	32(12)	-21(10)
C(44')	142(17)	84(13)	55(6)	13(7)	19(8)	-36(10)
O(50)	66(2)	43(2)	82(2)	12(1)	-33(2)	-9(1)
C(51)	43(5)	63(6)	75(8)	1(5)	0(5)	-7(4)
C(52)	64(8)	138(16)	153(18)	100(15)	-39(11)	-48(9)
C(53)	66(7)	27(7)	63(9)	-2(6)	22(7)	9(5)
C(54)	45(6)	52(9)	58(9)	-5(7)	-24(6)	-25(5)
C(51')	79(7)	35(4)	71(6)	5(3)	-37(5)	-2(4)
C(52')	66(7)	48(4)	47(5)	8(3)	6(4)	-8(4)
C(53')	113(9)	26(6)	42(5)	-13(5)	-31(5)	12(5)
C(54')	94(8)	46(6)	32(5)	-1(5)	-23(4)	-7(5)
O(60)	68(2)	65(2)	40(2)	-1(1)	10(1)	15(2)
C(61)	137(21)	99(11)	88(18)	4(13)	71(16)	0(12)
C(62)	92(15)	91(13)	154(22)	-79(13)	77(15)	-62(11)
C(63)	107(22)	96(11)	114(27)	-48(18)	82(22)	-1(14)
C(64)	90(17)	56(7)	336(47)	-76(14)	146(25)	-52(10)
C(61')	197(12)	119(9)	33(4)	-1(4)	24(5)	49(7)
C(62')	68(6)	144(11)	65(5)	-38(6)	32(4)	-10(6)
C(63')	63(5)	83(6)	94(7)	-37(5)	5(5)	15(4)
C(64')	87(6)	58(5)	62(4)	0(4)	13(4)	30(5)
O(70)	49(2)	88(2)	45(2)	-24(2)	-3(1)	-2(2)
C(71)	48(5)	131(11)	59(8)	-43(8)	8(5)	-1(6)
C(72)	102(8)	79(9)	35(8)	-28(6)	11(6)	-12(7)
C(73)	91(8)	60(9)	40(7)	-1(6)	-15(6)	-10(7)
C(74)	185(14)	75(11)	62(10)	-20(7)	-75(9)	69(9)
C(71')	42(4)	74(6)	35(4)	10(4)	12(3)	9(4)
C(72')	122(9)	65(8)	30(6)	-17(5)	12(6)	-9(6)
C(73')	96(8)	56(8)	48(7)	-3(6)	-34(6)	-8(7)
C(74')	29(3)	42(5)	31(4)	14(3)	-7(3)	15(3)

Table A-2d. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3-6b**.

	x	y	z	U(eq)
H(1'A)	430 (1)	4450 (2)	-805 (3)	85
H(1'B)	629 (1)	4242 (2)	-43 (3)	85
H(1'C)	342 (1)	4994 (2)	-41 (3)	85
H(2'A)	392 (1)	4250 (3)	1313 (2)	86
H(2'B)	314 (1)	3303 (3)	1748 (2)	86
H(2'C)	45 (1)	4108 (3)	1715 (2)	86
H(3'A)	-509 (1)	1853 (3)	1158 (2)	67
H(3'B)	-458 (1)	2797 (3)	1620 (2)	67
H(3'C)	-190 (1)	1992 (3)	1674 (2)	67
H(4'A)	-607 (1)	1601 (2)	-3 (2)	60
H(4'B)	-408 (1)	1484 (2)	-778 (2)	60
H(4'C)	-666 (1)	2310 (2)	-687 (2)	60
H(5'A)	119 (1)	3709 (3)	-1567 (2)	75
H(5'B)	-266 (1)	3511 (3)	-1540 (2)	75
H(5'C)	-15 (1)	2674 (3)	-1658 (2)	75
H(6A)	927 (1)	2246 (2)	-504 (2)	43
H(7A)	879 (1)	2230 (2)	965 (2)	50
H(8A)	457 (1)	963 (2)	1334 (2)	44
H(9A)	250 (1)	197 (2)	99 (2)	34
H(11A)	628 (1)	1345 (2)	-2395 (2)	73
H(11L)	848 (1)	1845 (2)	-1766 (2)	73
H(11M)	466 (1)	2065 (2)	-1817 (2)	73
H(12K)	222 (1)	143 (3)	-2017 (2)	63
H(12L)	56 (1)	851 (3)	-1435 (2)	63
H(12M)	180 (1)	-139 (3)	-1145 (2)	63
H(15A)	746 (1)	-247 (2)	-2524 (2)	36
H(16A)	1134 (1)	-1384 (2)	-2666 (2)	34
H(18A)	1392 (1)	-1088 (2)	-484 (2)	36
H(19A)	1002 (1)	34 (2)	-329 (2)	35
H(21A)	1194 (1)	-3028 (2)	-2655 (2)	43
H(22C)	1254 (1)	-3614 (3)	-3872 (2)	59
H(23C)	1763 (1)	-3587 (3)	-4461 (2)	74
H(24A)	2209 (1)	-2992 (3)	-3815 (2)	79
H(25A)	2149 (1)	-2375 (3)	-2594 (2)	53
H(27A)	1960 (1)	-2356 (3)	-254 (2)	58
H(28A)	2374 (1)	-1457 (4)	268 (3)	80
H(29A)	2624 (1)	-303 (3)	-420 (3)	82
H(30A)	2436 (1)	21 (3)	-1633 (3)	74
H(31A)	2008 (1)	-815 (2)	-2148 (2)	54
H(33A)	1908 (1)	-3854 (2)	-1301 (2)	48
H(34A)	1776 (1)	-5142 (3)	-583 (2)	58
H(35A)	1280 (1)	-5215 (3)	67 (2)	62
H(36A)	918 (1)	-3982 (3)	-22 (2)	55
H(37A)	1050 (1)	-2685 (2)	-734 (2)	42
H(41A)	1177 (6)	6221 (14)	1495 (8)	109
H(41B)	862 (6)	6804 (14)	1756 (8)	109
H(42A)	644 (5)	5604 (12)	2355 (14)	119
H(42B)	881 (5)	4999 (12)	1821 (14)	119
H(43A)	1265 (4)	4850 (10)	2744 (9)	73
H(43B)	940 (4)	4874 (10)	3262 (9)	73
H(44A)	1001 (5)	6395 (8)	3539 (5)	67

H (44B)	1379 (5)	6093 (8)	3487 (5)	67
H (41C)	1150 (4)	6736 (10)	1415 (6)	68
H (41D)	816 (4)	6868 (10)	1885 (6)	68
H (42C)	1181 (4)	5193 (10)	1709 (7)	91
H (42D)	794 (4)	5329 (10)	1581 (7)	91
H (43C)	690 (6)	5384 (11)	2845 (9)	102
H (43D)	999 (6)	4690 (11)	2852 (9)	102
H (44C)	999 (6)	6332 (11)	3516 (8)	113
H (44D)	1325 (6)	5762 (11)	3317 (8)	113
H (51A)	2043 (2)	8654 (7)	1374 (7)	72
H (51B)	1985 (2)	9225 (7)	2142 (7)	72
H (52A)	1874 (3)	10416 (12)	1453 (13)	142
H (52B)	1880 (3)	9804 (12)	694 (13)	142
H (53A)	1350 (3)	10056 (10)	653 (12)	62
H (53B)	1336 (3)	10346 (10)	1538 (12)	62
H (54A)	1136 (3)	8934 (9)	1666 (11)	62
H (54B)	1305 (3)	8575 (9)	903 (11)	62
H (51C)	1952 (3)	9237 (3)	2313 (5)	74
H (51D)	1590 (3)	9514 (3)	2594 (5)	74
H (52C)	1892 (3)	9976 (6)	1195 (5)	64
H (52D)	1663 (3)	10628 (6)	1716 (5)	64
H (53C)	1434 (3)	9745 (8)	567 (9)	73
H (53D)	1211 (3)	10017 (8)	1279 (9)	73
H (54C)	1117 (3)	8558 (8)	1477 (8)	69
H (54D)	1366 (3)	8280 (8)	801 (8)	69
H (61A)	2285 (5)	7342 (10)	1780 (16)	129
H (61B)	2045 (5)	7290 (10)	1062 (16)	129
H (62A)	2591 (5)	6321 (12)	1230 (15)	135
H (62B)	2323 (5)	6163 (12)	575 (15)	135
H (63A)	2211 (5)	4842 (14)	1104 (18)	126
H (63B)	2431 (5)	5088 (14)	1831 (18)	126
H (64A)	1768 (6)	5200 (4)	1707 (24)	193
H (64B)	1985 (6)	5301 (4)	2463 (24)	193
H (61C)	2101 (3)	7122 (9)	1026 (3)	139
H (61D)	1807 (3)	6428 (9)	821 (3)	139
H (62C)	2438 (2)	5998 (9)	784 (4)	111
H (62D)	2142 (2)	5269 (9)	711 (4)	111
H (63C)	2501 (3)	5733 (8)	2021 (5)	96
H (63D)	2352 (3)	4738 (8)	1792 (5)	96
H (64C)	1840 (2)	5147 (4)	2144 (5)	83
H (64D)	2055 (2)	5675 (4)	2777 (5)	83
H (71A)	1387 (2)	8362 (8)	3821 (8)	96
H (71B)	1627 (2)	9068 (8)	3374 (8)	96
H (72A)	1696 (4)	8376 (19)	4846 (11)	86
H (72B)	1853 (4)	9295 (19)	4506 (11)	86
H (73A)	2336 (6)	8617 (17)	4318 (10)	76
H (73B)	2201 (6)	7848 (17)	4913 (10)	76
H (74A)	2279 (3)	7542 (11)	3416 (9)	129
H (74B)	2081 (3)	6872 (11)	3976 (9)	129
H (71C)	1544 (2)	7479 (8)	4345 (4)	60
H (71D)	1405 (2)	8341 (8)	3874 (4)	60
H (72C)	1817 (4)	9321 (16)	4330 (11)	87
H (72D)	1733 (4)	8693 (16)	5073 (11)	87
H (73C)	2102 (5)	7553 (17)	4721 (8)	80
H (73D)	2303 (5)	8478 (17)	4542 (8)	80
H (74C)	2245 (1)	8307 (7)	3263 (5)	41
H (74D)	2254 (1)	7231 (7)	3517 (5)	41

Table A-3a. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 4-1. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Zr	7622 (1)	2850 (1)	1852 (1)	17 (1)
Br	-2517 (1)	8649 (1)	4725 (1)	35 (1)
C11	6947 (1)	5735 (1)	1182 (1)	27 (1)
C12	9781 (1)	2776 (1)	2734 (1)	35 (1)
C1	5302 (3)	4077 (3)	2911 (1)	21 (1)
C2	4379 (3)	4612 (3)	2226 (1)	22 (1)
C3	4524 (3)	3139 (3)	1912 (2)	27 (1)
C4	5527 (3)	1661 (3)	2410 (2)	29 (1)
C5	6013 (3)	2243 (3)	3014 (1)	26 (1)
C6	5235 (3)	5286 (3)	3471 (1)	23 (1)
C7	6380 (4)	4237 (4)	4160 (1)	32 (1)
C8	5949 (3)	6615 (3)	3127 (2)	26 (1)
C9	3272 (3)	6183 (3)	3732 (1)	22 (1)
C10	2517 (4)	7889 (3)	3902 (1)	28 (1)
C11	790 (4)	8643 (3)	4181 (2)	29 (1)
C12	-184 (3)	7664 (3)	4302 (1)	26 (1)
C13	506 (4)	5977 (3)	4127 (2)	30 (1)
C14	2214 (4)	5259 (3)	3846 (2)	30 (1)
C21	9150 (3)	-186 (3)	1509 (1)	22 (1)
C21'	9268 (4)	-1786 (3)	2004 (2)	33 (1)
C22	7864 (3)	769 (3)	938 (1)	23 (1)
C22'	6390 (4)	339 (4)	706 (2)	34 (1)
C23	8383 (3)	2023 (3)	544 (1)	21 (1)
C23'	7537 (4)	3179 (4)	-149 (2)	31 (1)
C24	10001 (3)	1839 (3)	867 (1)	20 (1)
C24'	11060 (3)	2870 (3)	618 (2)	28 (1)
C25	10487 (3)	451 (3)	1446 (1)	21 (1)
C25'	12217 (3)	-328 (3)	1858 (2)	27 (1)

Table A-3b. Bond lengths [Å] and angles [deg] for 4-1.

Zr-Cl2	2.4373 (6)
Zr-Cl1	2.4585 (6)
Zr-C3	2.464 (2)
Zr-C4	2.468 (2)
Zr-C21	2.513 (2)
Zr-C22	2.529 (2)
Zr-C24	2.531 (2)
Zr-C23	2.539 (2)
Zr-C25	2.545 (2)
Zr-C5	2.547 (2)
Zr-C2	2.566 (2)
Zr-C1	2.629 (2)
Br-Cl2	1.912 (2)
Cl1-C2	1.416 (3)
Cl1-C5	1.417 (3)
Cl1-C6	1.524 (3)
C2-C3	1.408 (3)
C2-H2	0.87 (3)
C3-C4	1.419 (4)
C3-H3	0.89 (3)
C4-C5	1.403 (4)
C4-H4	0.94 (3)
C5-H5	0.97 (3)
C6-C8	1.542 (3)
C6-C7	1.548 (3)
C6-C9	1.551 (3)
C7-H7A	0.96 (3)
C7-H7B	0.99 (3)
C7-H7C	1.00 (3)
C8-H8A	1.01 (3)
C8-H8B	1.02 (3)
C8-H8C	0.95 (3)
C9-C10	1.396 (3)
C9-C14	1.398 (3)
C10-C11	1.393 (4)
C10-H10	0.97 (3)
C11-C12	1.378 (4)
C11-H11	0.98 (3)
C12-C13	1.386 (4)
C13-C14	1.379 (4)
C13-H13	0.84 (3)
C14-H14	0.96 (3)
C21-C25	1.417 (3)
C21-C22	1.430 (3)
C21-C21'	1.509 (3)
C21'-H21A	0.96 (4)
C21'-H21B	0.92 (4)
C21'-H21C	0.98 (3)
C22-C23	1.417 (3)
C22-C22'	1.507 (3)
C22'-H22A	0.91 (4)
C22'-H22B	0.96 (4)
C22'-H22C	0.95 (4)
C23-C24	1.429 (3)
C23-C23'	1.499 (3)

C23'-H23A	1.05 (4)
C23'-H23B	0.97 (4)
C23'-H23C	1.03 (4)
C24-C25	1.417 (3)
C24-C24'	1.502 (3)
C24'-H24A	0.93 (3)
C24'-H24B	0.89 (4)
C24'-H24C	0.99 (3)
C25-C25'	1.495 (3)
C25'-H25A	0.98 (3)
C25'-H25B	0.88 (3)
C25'-H25C	0.95 (3)
C12-Zr-C11	98.48 (2)
C12-Zr-C3	135.96 (6)
C11-Zr-C3	96.17 (7)
C12-Zr-C4	113.38 (7)
C11-Zr-C4	128.58 (7)
C3-Zr-C4	33.44 (9)
C12-Zr-C21	99.82 (6)
C11-Zr-C21	134.18 (6)
C3-Zr-C21	99.04 (8)
C4-Zr-C21	80.20 (8)
C12-Zr-C22	130.80 (6)
C11-Zr-C22	109.51 (6)
C3-Zr-C22	81.12 (8)
C4-Zr-C22	79.39 (8)
C21-Zr-C22	32.96 (8)
C12-Zr-C24	91.62 (5)
C11-Zr-C24	83.67 (5)
C3-Zr-C24	131.27 (8)
C4-Zr-C24	131.66 (8)
C21-Zr-C24	54.25 (7)
C22-Zr-C24	54.03 (7)
C12-Zr-C23	124.36 (5)
C11-Zr-C23	80.75 (5)
C3-Zr-C23	98.88 (8)
C4-Zr-C23	109.14 (8)
C21-Zr-C23	54.35 (8)
C22-Zr-C23	32.47 (7)
C24-Zr-C23	32.75 (7)
C12-Zr-C25	78.04 (5)
C11-Zr-C25	114.58 (5)
C3-Zr-C25	131.14 (8)
C4-Zr-C25	110.92 (8)
C21-Zr-C25	32.55 (7)
C22-Zr-C25	53.85 (7)
C24-Zr-C25	32.41 (7)
C23-Zr-C25	53.85 (7)
C12-Zr-C5	83.97 (6)
C11-Zr-C5	125.11 (6)
C3-Zr-C5	54.05 (9)
C4-Zr-C5	32.44 (8)
C21-Zr-C5	98.40 (8)
C22-Zr-C5	109.21 (8)
C24-Zr-C5	151.21 (7)
C23-Zr-C5	140.87 (8)
C25-Zr-C5	119.45 (8)

C12-Zr-C2	113.03 (5)
C11-Zr-C2	77.25 (6)
C3-Zr-C2	32.44 (8)
C4-Zr-C2	53.84 (8)
C21-Zr-C2	130.76 (8)
C22-Zr-C2	112.14 (7)
C24-Zr-C2	150.59 (7)
C23-Zr-C2	120.68 (7)
C25-Zr-C2	163.29 (8)
C5-Zr-C2	52.69 (8)
C12-Zr-C1	84.12 (5)
C11-Zr-C1	93.59 (5)
C3-Zr-C1	53.61 (8)
C4-Zr-C1	53.53 (8)
C21-Zr-C1	129.79 (7)
C22-Zr-C1	131.41 (7)
C24-Zr-C1	174.56 (7)
C23-Zr-C1	151.41 (7)
C25-Zr-C1	148.39 (7)
C5-Zr-C1	31.73 (7)
C2-Zr-C1	31.61 (7)
C2-C1-C5	106.4 (2)
C2-C1-C6	124.9 (2)
C5-C1-C6	127.9 (2)
C2-C1-Zr	71.74 (13)
C5-C1-Zr	70.97 (13)
C6-C1-Zr	129.9 (2)
C3-C2-C1	109.1 (2)
C3-C2-Zr	69.79 (13)
C1-C2-Zr	76.65 (13)
C3-C2-H2	125 (2)
C1-C2-H2	126 (2)
Zr-C2-H2	120 (2)
C2-C3-C4	107.6 (2)
C2-C3-Zr	77.77 (14)
C4-C3-Zr	73.45 (14)
C2-C3-H3	128 (2)
C4-C3-H3	125 (2)
Zr-C3-H3	119 (2)
C5-C4-C3	107.6 (2)
C5-C4-Zr	76.89 (14)
C3-C4-Zr	73.11 (14)
C5-C4-H4	123 (2)
C3-C4-H4	130 (2)
Zr-C4-H4	113 (2)
C4-C5-C1	109.3 (2)
C4-C5-Zr	70.67 (14)
C1-C5-Zr	77.30 (13)
C4-C5-H5	126 (2)
C1-C5-H5	125 (2)
Zr-C5-H5	119 (2)
C1-C6-C8	111.0 (2)
C1-C6-C7	110.3 (2)
C8-C6-C7	108.4 (2)
C1-C6-C9	107.6 (2)
C8-C6-C9	111.8 (2)
C7-C6-C9	107.7 (2)
C6-C7-H7A	110 (2)

C6-C7-H7B	110 (2)
H7A-C7-H7B	109 (2)
C6-C7-H7C	110 (2)
H7A-C7-H7C	108 (2)
H7B-C7-H7C	110 (2)
C6-C8-H8A	113 (2)
C6-C8-H8B	112 (2)
H8A-C8-H8B	105 (2)
C6-C8-H8C	111 (2)
H8A-C8-H8C	111 (2)
H8B-C8-H8C	105 (2)
C10-C9-C14	117.2 (2)
C10-C9-C6	122.3 (2)
C14-C9-C6	120.4 (2)
C11-C10-C9	121.7 (2)
C11-C10-H10	117 (2)
C9-C10-H10	122 (2)
C12-C11-C10	118.9 (2)
C12-C11-H11	121 (2)
C10-C11-H11	120 (2)
C11-C12-C13	121.0 (2)
C11-C12-Br	119.4 (2)
C13-C12-Br	119.6 (2)
C14-C13-C12	119.1 (2)
C14-C13-H13	121 (2)
C12-C13-H13	120 (2)
C13-C14-C9	122.0 (2)
C13-C14-H14	121 (2)
C9-C14-H14	117 (2)
C25-C21-C22	107.6 (2)
C25-C21-C21'	124.8 (2)
C22-C21-C21'	126.8 (2)
C25-C21-Zr	74.98 (12)
C22-C21-Zr	74.16 (13)
C21'-C21-Zr	124.7 (2)
C21-C21'-H21A	112 (2)
C21-C21'-H21B	112 (2)
H21A-C21'-H21B	114 (3)
C21-C21'-H21C	111 (2)
H21A-C21'-H21C	106 (3)
H21B-C21'-H21C	101 (3)
C23-C22-C21	108.2 (2)
C23-C22-C22'	124.8 (2)
C21-C22-C22'	126.2 (2)
C23-C22-Zr	74.14 (13)
C21-C22-Zr	72.87 (13)
C22'-C22-Zr	126.6 (2)
C22-C22'-H22A	116 (3)
C22-C22'-H22B	110 (2)
H22A-C22'-H22B	111 (3)
C22-C22'-H22C	109 (2)
H22A-C22'-H22C	99 (3)
H22B-C22'-H22C	113 (3)
C22-C23-C24	107.7 (2)
C22-C23-C23'	126.5 (2)
C24-C23-C23'	125.4 (2)
C22-C23-Zr	73.39 (13)
C24-C23-Zr	73.30 (13)

C23'-C23-Zr	125.0 (2)
C23-C23'-H23A	116 (2)
C23-C23'-H23B	108 (2)
H23A-C23'-H23B	112 (3)
C23-C23'-H23C	111 (2)
H23A-C23'-H23C	102 (3)
H23B-C23'-H23C	107 (3)
C25-C24-C23	108.0 (2)
C25-C24-C24'	125.5 (2)
C23-C24-C24'	126.4 (2)
C25-C24-Zr	74.35 (13)
C23-C24-Zr	73.95 (12)
C24'-C24-Zr	119.9 (2)
C24-C24'-H24A	117 (2)
C24-C24'-H24B	112 (2)
H24A-C24'-H24B	111 (3)
C24-C24'-H24C	112 (2)
H24A-C24'-H24C	101 (3)
H24B-C24'-H24C	103 (3)
C24-C25-C21	108.4 (2)
C24-C25-C25'	125.2 (2)
C21-C25-C25'	126.0 (2)
C24-C25-Zr	73.24 (12)
C21-C25-Zr	72.47 (12)
C25'-C25-Zr	125.5 (2)
C25-C25'-H25A	110 (2)
C25-C25'-H25B	113 (2)
H25A-C25'-H25B	107 (3)
C25-C25'-H25C	111 (2)
H25A-C25'-H25C	111 (3)
H25B-C25'-H25C	105 (3)

Symmetry transformations used to generate equivalent atoms:

Table A-3c. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 4-1. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Zr	15(1)	15(1)	20(1)	-4(1)	1(1)	-6(1)
Br	29(1)	33(1)	38(1)	-8(1)	10(1)	-8(1)
C11	32(1)	18(1)	32(1)	-2(1)	6(1)	-10(1)
C12	23(1)	44(1)	36(1)	-17(1)	-4(1)	-9(1)
C1	20(1)	20(1)	21(1)	-2(1)	4(1)	-8(1)
C2	17(1)	24(1)	23(1)	-5(1)	1(1)	-5(1)
C3	19(1)	37(1)	31(1)	-15(1)	5(1)	-14(1)
C4	27(1)	25(1)	40(2)	-11(1)	12(1)	-16(1)
C5	28(1)	21(1)	26(1)	1(1)	8(1)	-9(1)
C6	24(1)	25(1)	19(1)	-4(1)	1(1)	-9(1)
C7	35(2)	39(1)	19(1)	-2(1)	-1(1)	-10(1)
C8	26(1)	29(1)	28(1)	-9(1)	4(1)	-14(1)
C9	27(1)	23(1)	16(1)	-3(1)	2(1)	-10(1)
C10	32(1)	28(1)	28(1)	-7(1)	6(1)	-15(1)
C11	33(1)	24(1)	29(1)	-9(1)	5(1)	-9(1)
C12	24(1)	29(1)	22(1)	-6(1)	6(1)	-7(1)
C13	33(1)	28(1)	33(1)	-7(1)	9(1)	-16(1)
C14	34(1)	23(1)	30(1)	-8(1)	7(1)	-11(1)
C21	20(1)	16(1)	30(1)	-7(1)	5(1)	-7(1)
C21'	33(2)	19(1)	47(2)	-2(1)	7(1)	-11(1)
C22	20(1)	23(1)	28(1)	-12(1)	3(1)	-7(1)
C22'	26(1)	36(2)	48(2)	-23(1)	4(1)	-15(1)
C23	18(1)	22(1)	23(1)	-9(1)	2(1)	-6(1)
C23'	31(1)	32(1)	24(1)	-5(1)	-4(1)	-7(1)
C24	16(1)	18(1)	23(1)	-6(1)	3(1)	-6(1)
C24'	23(1)	26(1)	36(2)	-2(1)	6(1)	-11(1)
C25	17(1)	15(1)	28(1)	-5(1)	1(1)	-4(1)
C25'	18(1)	25(1)	33(1)	-3(1)	-2(1)	-5(1)

Table A-3d. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4-1**.

	x	y	z	U(eq)
H2	3815 (38)	5671 (38)	2025 (16)	26 (7)
H3	4016 (37)	3110 (34)	1500 (16)	24 (7)
H4	5906 (40)	473 (39)	2363 (16)	35 (8)
H5	6708 (38)	1514 (37)	3436 (16)	28 (7)
H7A	5948 (39)	3414 (39)	4387 (16)	32 (8)
H7B	6308 (39)	5031 (39)	4521 (17)	35 (8)
H7C	7646 (39)	3587 (37)	4008 (15)	29 (7)
H8A	5267 (36)	7345 (36)	2671 (15)	27 (7)
H8B	7236 (39)	6036 (37)	2953 (16)	29 (7)
H8C	5962 (33)	7326 (33)	3484 (14)	16 (6)
H10	3166 (42)	8611 (41)	3827 (17)	42 (9)
H11	332 (38)	9814 (39)	4323 (16)	30 (7)
H13	-102 (40)	5391 (39)	4213 (16)	33 (8)
H14	2728 (42)	4098 (42)	3714 (17)	40 (8)
H21A	9471 (50)	-1733 (48)	2512 (22)	58 (11)
H21B	10053 (52)	-2787 (53)	1827 (22)	68 (12)
H21C	8151 (45)	-1922 (40)	1995 (17)	42 (9)
H22A	5738 (53)	85 (51)	1083 (22)	62 (12)
H22B	6864 (50)	-569 (51)	386 (21)	64 (11)
H22C	5479 (51)	1365 (51)	474 (20)	59 (11)
H23A	7486 (46)	4433 (47)	-193 (19)	56 (10)
H23B	8127 (49)	2589 (47)	-571 (20)	57 (10)
H23C	6211 (50)	3423 (45)	-180 (19)	58 (11)
H24A	10939 (43)	3753 (43)	897 (18)	43 (9)
H24B	10919 (44)	3251 (44)	135 (20)	49 (10)
H24C	12353 (46)	2150 (43)	664 (18)	43 (9)
H25A	12097 (38)	-965 (38)	2332 (17)	31 (7)
H25B	12575 (38)	451 (38)	1962 (15)	28 (7)
H25C	13156 (43)	-1065 (41)	1566 (17)	37 (8)

Table A-4a. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 4-3. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Zr	7500 (1)	864 (1)	-2490 (1)	22 (1)
Br1	10050 (1)	-2924 (1)	1355 (1)	53 (1)
Br2	5051 (1)	-2909 (1)	-6396 (1)	48 (1)
C11	7952 (1)	2121 (1)	-3090 (1)	33 (1)
C12	7082 (1)	2126 (1)	-1874 (1)	34 (1)
C1	8191 (2)	164 (3)	-1289 (2)	24 (1)
C2	8609 (2)	919 (3)	-1438 (2)	28 (1)
C3	8799 (2)	586 (3)	-1989 (2)	31 (1)
C4	8481 (2)	-339 (3)	-2211 (2)	30 (1)
C5	8107 (2)	-605 (3)	-1777 (2)	24 (1)
C6	7992 (2)	85 (3)	-650 (2)	30 (1)
C7	8125 (3)	1087 (4)	-253 (3)	44 (1)
C8	7219 (3)	-216 (4)	-846 (3)	42 (1)
C9	8487 (2)	-695 (3)	-169 (2)	29 (1)
C10	8306 (3)	-1215 (3)	322 (2)	38 (1)
C11	8766 (3)	-1865 (3)	774 (2)	38 (1)
C12	9423 (3)	-2000 (3)	750 (2)	36 (1)
C13	9626 (3)	-1495 (4)	275 (2)	42 (1)
C14	9159 (2)	-847 (4)	-179 (2)	39 (1)
C21	6798 (2)	202 (3)	-3706 (2)	22 (1)
C22	6873 (2)	-576 (3)	-3225 (2)	25 (1)
C23	6502 (2)	-313 (3)	-2787 (2)	27 (1)
C24	6202 (2)	626 (3)	-2993 (2)	32 (1)
C25	6391 (2)	959 (3)	-3541 (2)	30 (1)
C26	7016 (2)	135 (3)	-4333 (2)	29 (1)
C27	6894 (3)	1142 (4)	-4729 (3)	39 (1)
C28	7794 (2)	-158 (4)	-4128 (3)	35 (1)
C29	6537 (2)	-633 (3)	-4829 (2)	30 (1)
C30	6758 (3)	-1179 (3)	-5286 (2)	32 (1)
C31	6322 (3)	-1837 (3)	-5756 (2)	37 (1)
C32	5653 (2)	-1971 (3)	-5772 (2)	32 (1)
C33	5409 (3)	-1445 (4)	-5333 (3)	48 (1)
C34	5853 (3)	-785 (4)	-4870 (2)	44 (1)
Zr'	7379 (1)	-4217 (1)	2384 (1)	19 (1)
Br1'	11524 (1)	-7530 (1)	4912 (1)	42 (1)
Br2'	3669 (1)	-8243 (1)	-376 (1)	35 (1)
C11'	7928 (1)	-2875 (1)	1954 (1)	29 (1)
C12'	6635 (1)	-3072 (1)	2741 (1)	31 (1)
C1'	8659 (2)	-4735 (3)	3101 (2)	20 (1)
C2'	8445 (2)	-3988 (3)	3480 (2)	24 (1)
C3'	7888 (2)	-4372 (3)	3664 (2)	25 (1)
C4'	7730 (2)	-5337 (3)	3376 (2)	25 (1)
C5'	8200 (2)	-5554 (3)	3033 (2)	23 (1)
C6'	9304 (2)	-4724 (3)	2894 (2)	27 (1)
C7'	9637 (3)	-3672 (3)	2973 (3)	31 (1)
C8'	9114 (3)	-5048 (4)	2144 (2)	33 (1)
C9'	9842 (2)	-5440 (3)	3382 (2)	24 (1)
C10'	10131 (2)	-5215 (3)	4081 (2)	31 (1)
C11'	10626 (2)	-5822 (3)	4537 (2)	33 (1)
C12'	10840 (2)	-6674 (3)	4296 (2)	30 (1)

C13'	10575 (2)	-6915 (3)	3607 (2)	31 (1)
C14'	10074 (2)	-6307 (3)	3164 (2)	30 (1)
C21'	6207 (2)	-5080 (3)	1667 (2)	19 (1)
C22'	6766 (2)	-5775 (3)	1815 (2)	22 (1)
C23'	7224 (2)	-5461 (3)	1470 (2)	28 (1)
C24'	6952 (3)	-4580 (3)	1120 (2)	33 (1)
C25'	6346 (2)	-4321 (3)	1256 (2)	26 (1)
C26'	5531 (2)	-5252 (3)	1806 (2)	24 (1)
C27'	5084 (3)	-4299 (3)	1691 (3)	36 (1)
C28'	5695 (3)	-5616 (4)	2544 (2)	33 (1)
C29'	5097 (2)	-6037 (3)	1280 (2)	21 (1)
C30'	4481 (2)	-6413 (3)	1332 (2)	27 (1)
C31'	4050 (2)	-7071 (3)	847 (2)	29 (1)
C32'	4246 (2)	-7360 (3)	303 (2)	25 (1)
C33'	4849 (2)	-7014 (3)	239 (2)	27 (1)
C34'	5274 (2)	-6342 (3)	728 (2)	27 (1)

Table A-4b. Bond lengths [Å] and angles [deg] for 4-3.

Zr-C12	2.4477 (10)
Zr-C11	2.4587 (10)
Zr-C4	2.473 (4)
Zr-C23	2.474 (4)
Zr-C24	2.498 (4)
Zr-C3	2.510 (4)
Zr-C5	2.515 (4)
Zr-C22	2.515 (4)
Zr-C25	2.539 (4)
Zr-C2	2.540 (4)
Zr-C1	2.580 (4)
Zr-C21	2.590 (4)
Br1-C12	1.904 (4)
Br2-C32	1.911 (4)
C1-C5	1.415 (5)
C1-C2	1.424 (5)
C1-C6	1.523 (5)
C2-C3	1.407 (6)
C2-H2	0.95 (3)
C3-C4	1.400 (6)
C3-H3	0.92 (3)
C4-C5	1.417 (6)
C4-H4	0.85 (4)
C5-H5	1.04 (3)
C6-C8	1.536 (6)
C6-C7	1.550 (6)
C6-C9	1.552 (5)
C7-H7A	1.07 (4)
C7-H7B	1.03 (5)
C7-H7C	0.94 (4)
C8-H8A	0.98 (4)
C8-H8B	0.93 (4)
C8-H8C	1.00 (4)
C9-C10	1.389 (5)
C9-C14	1.390 (6)
C10-C11	1.381 (6)
C10-H10	0.94 (4)
C11-C12	1.367 (6)
C11-H11	0.87 (4)
C12-C13	1.377 (6)
C13-C14	1.388 (6)
C13-H13	0.93 (4)
C14-H14	0.95 (4)
C21-C22	1.415 (5)
C21-C25	1.426 (5)
C21-C26	1.522 (5)
C22-C23	1.419 (5)
C22-H22	0.97 (4)
C23-C24	1.398 (6)
C23-H23	0.87 (3)
C24-C25	1.398 (6)
C24-H24	0.94 (4)
C25-H25	0.95 (3)
C26-C28	1.540 (6)
C26-C29	1.540 (5)

C26-C27	1.556 (6)
C27-H27A	0.89 (4)
C27-H27B	0.94 (4)
C27-H27C	1.08 (5)
C28-H28A	0.98 (3)
C28-H28B	0.92 (4)
C28-H28C	0.99 (4)
C29-C34	1.380 (6)
C29-C30	1.394 (5)
C30-C31	1.384 (6)
C30-H30	0.87 (3)
C31-C32	1.364 (6)
C31-H31	0.91 (4)
C32-C33	1.375 (6)
C33-C34	1.385 (6)
C33-H33	0.83 (4)
C34-H34	0.84 (3)
Zr'-C11'	2.4456 (10)
Zr'-C12'	2.4487 (10)
Zr'-C4'	2.450 (4)
Zr'-C23'	2.465 (4)
Zr'-C5'	2.500 (4)
Zr'-C22'	2.507 (4)
Zr'-C3'	2.509 (4)
Zr'-C24'	2.513 (4)
Zr'-C25'	2.551 (4)
Zr'-C2'	2.560 (4)
Zr'-C21'	2.602 (4)
Zr'-C1'	2.604 (4)
Br1'-C12'	1.910 (4)
Br2'-C32'	1.902 (4)
C1'-C5'	1.415 (5)
C1'-C2'	1.435 (5)
C1'-C6'	1.518 (5)
C2'-C3'	1.414 (6)
C2'-H2'	0.93 (3)
C3'-C4'	1.414 (5)
C3'-H3'	0.98 (4)
C4'-C5'	1.410 (6)
C4'-H4'	0.91 (3)
C5'-H5'	0.87 (3)
C6'-C8'	1.536 (5)
C6'-C9'	1.541 (5)
C6'-C7'	1.547 (5)
C7'-H7D	1.07 (4)
C7'-H7E	0.98 (4)
C7'-H7F	0.89 (4)
C8'-H8D	1.00 (4)
C8'-H8E	0.87 (4)
C8'-H8F	1.00 (4)
C9'-C14'	1.389 (5)
C9'-C10'	1.399 (5)
C10'-C11'	1.380 (6)
C10'-H10'	0.99 (3)
C11'-C12'	1.378 (5)
C11'-H11'	0.93 (4)
C12'-C13'	1.383 (5)
C13'-C14'	1.377 (6)

C13'-H13'	0.93 (4)
C14'-H14'	0.92 (3)
C21'-C22'	1.419 (5)
C21'-C25'	1.419 (5)
C21'-C26'	1.518 (5)
C22'-C23'	1.425 (6)
C22'-H22'	1.00 (4)
C23'-C24'	1.395 (6)
C23'-H23'	0.82 (3)
C24'-C25'	1.403 (6)
C24'-H24'	0.82 (3)
C25'-H25'	1.01 (4)
C26'-C28'	1.535 (6)
C26'-C27'	1.537 (5)
C26'-C29'	1.552 (5)
C27'-H27D	1.06 (4)
C27'-H27E	0.99 (4)
C27'-H27F	0.93 (4)
C28'-H28D	0.90 (4)
C28'-H28E	1.05 (5)
C28'-H28F	0.88 (4)
C29'-C34'	1.383 (5)
C29'-C30'	1.390 (5)
C30'-C31'	1.395 (5)
C30'-H30'	0.90 (4)
C31'-C32'	1.382 (5)
C31'-H31'	0.90 (4)
C32'-C33'	1.361 (5)
C33'-C34'	1.407 (5)
C33'-H33'	0.96 (3)
C34'-H34'	0.94 (4)
C12-Zr-C11	93.09 (3)
C12-Zr-C4	136.66 (10)
C11-Zr-C4	98.63 (11)
C12-Zr-C23	99.54 (10)
C11-Zr-C23	136.93 (10)
C4-Zr-C23	99.72 (14)
C12-Zr-C24	78.31 (11)
C11-Zr-C24	113.82 (11)
C4-Zr-C24	131.63 (14)
C23-Zr-C24	32.66 (13)
C12-Zr-C3	113.20 (11)
C11-Zr-C3	77.56 (10)
C4-Zr-C3	32.62 (13)
C23-Zr-C3	131.59 (14)
C24-Zr-C3	164.13 (14)
C12-Zr-C5	114.84 (9)
C11-Zr-C5	129.91 (10)
C4-Zr-C5	32.99 (13)
C23-Zr-C5	80.79 (14)
C24-Zr-C5	112.15 (14)
C3-Zr-C5	53.79 (14)
C12-Zr-C22	130.80 (10)
C11-Zr-C22	114.60 (10)
C4-Zr-C22	80.77 (14)
C23-Zr-C22	33.02 (13)
C24-Zr-C22	53.85 (14)

C3-Zr-C22	112.08(14)
C5-Zr-C22	78.44(12)
C12-Zr-C25	92.85(10)
C11-Zr-C25	84.62(11)
C4-Zr-C25	129.59(14)
C23-Zr-C25	53.95(14)
C24-Zr-C25	32.22(13)
C3-Zr-C25	148.89(14)
C5-Zr-C25	130.83(13)
C22-Zr-C25	53.48(13)
C12-Zr-C2	83.98(10)
C11-Zr-C2	92.32(10)
C4-Zr-C2	54.13(14)
C23-Zr-C2	129.70(14)
C24-Zr-C2	148.90(14)
C3-Zr-C2	32.36(13)
C5-Zr-C2	53.64(13)
C22-Zr-C2	131.00(13)
C25-Zr-C2	175.49(13)
C12-Zr-C1	85.08(9)
C11-Zr-C1	124.55(9)
C4-Zr-C1	54.09(13)
C23-Zr-C1	97.60(13)
C24-Zr-C1	119.86(13)
C3-Zr-C1	53.49(13)
C5-Zr-C1	32.21(11)
C22-Zr-C1	107.47(12)
C25-Zr-C1	150.80(13)
C2-Zr-C1	32.28(12)
C12-Zr-C21	125.08(9)
C11-Zr-C21	85.13(9)
C4-Zr-C21	97.52(13)
C23-Zr-C21	54.06(13)
C24-Zr-C21	53.52(13)
C3-Zr-C21	119.78(13)
C5-Zr-C21	107.38(12)
C22-Zr-C21	32.13(11)
C25-Zr-C21	32.26(12)
C2-Zr-C21	150.89(13)
C1-Zr-C21	138.65(11)
C5-C1-C2	106.9(4)
C5-C1-C6	125.0(3)
C2-C1-C6	127.0(3)
C5-C1-Zr	71.4(2)
C2-C1-Zr	72.3(2)
C6-C1-Zr	130.6(3)
C3-C2-C1	108.1(4)
C3-C2-Zr	72.6(2)
C1-C2-Zr	75.4(2)
C3-C2-H2	130(2)
C1-C2-H2	122(2)
Zr-C2-H2	116(2)
C4-C3-C2	108.7(4)
C4-C3-Zr	72.3(2)
C2-C3-Zr	75.0(2)
C4-C3-H3	122(2)
C2-C3-H3	129(2)
Zr-C3-H3	119(2)

C3-C4-C5	107.6(4)
C3-C4-Zr	75.1(2)
C5-C4-Zr	75.1(2)
C3-C4-H4	131(3)
C5-C4-H4	122(3)
Zr-C4-H4	118(3)
C1-C5-C4	108.6(4)
C1-C5-Zr	76.4(2)
C4-C5-Zr	71.9(2)
C1-C5-H5	126(2)
C4-C5-H5	126(2)
Zr-C5-H5	116(2)
C1-C6-C8	110.3(3)
C1-C6-C7	110.8(4)
C8-C6-C7	109.9(4)
C1-C6-C9	107.5(3)
C8-C6-C9	111.7(4)
C7-C6-C9	106.6(3)
C6-C7-H7A	111(2)
C6-C7-H7B	113(3)
H7A-C7-H7B	113(4)
C6-C7-H7C	106(3)
H7A-C7-H7C	116(3)
H7B-C7-H7C	96(4)
C6-C8-H8A	114(3)
C6-C8-H8B	113(3)
H8A-C8-H8B	100(4)
C6-C8-H8C	111(3)
H8A-C8-H8C	105(3)
H8B-C8-H8C	114(4)
C10-C9-C14	117.0(4)
C10-C9-C6	122.2(4)
C14-C9-C6	120.6(4)
C11-C10-C9	121.7(5)
C11-C10-H10	121(2)
C9-C10-H10	117(2)
C12-C11-C10	119.9(4)
C12-C11-H11	123(3)
C10-C11-H11	117(3)
C11-C12-C13	120.4(4)
C11-C12-Br1	120.0(3)
C13-C12-Br1	119.6(4)
C12-C13-C14	119.3(5)
C12-C13-H13	122(2)
C14-C13-H13	118(2)
C13-C14-C9	121.7(4)
C13-C14-H14	115(3)
C9-C14-H14	124(3)
C22-C21-C25	106.4(4)
C22-C21-C26	124.8(3)
C25-C21-C26	128.1(4)
C22-C21-Zr	71.0(2)
C25-C21-Zr	71.9(2)
C26-C21-Zr	129.2(3)
C21-C22-C23	108.8(4)
C21-C22-Zr	76.9(2)
C23-C22-Zr	71.9(2)
C21-C22-H22	123(2)

C23-C22-H22	129 (2)
Zr-C22-H22	120 (2)
C24-C23-C22	107.4 (4)
C24-C23-Zr	74.6 (2)
C22-C23-Zr	75.1 (2)
C24-C23-H23	127 (2)
C22-C23-H23	126 (2)
Zr-C23-H23	114 (2)
C25-C24-C23	108.8 (4)
C25-C24-Zr	75.5 (2)
C23-C24-Zr	72.7 (2)
C25-C24-H24	126 (2)
C23-C24-H24	124 (2)
Zr-C24-H24	112 (2)
C24-C25-C21	108.5 (4)
C24-C25-Zr	72.3 (2)
C21-C25-Zr	75.9 (2)
C24-C25-H25	126 (2)
C21-C25-H25	125 (2)
Zr-C25-H25	123 (2)
C21-C26-C28	111.0 (3)
C21-C26-C29	108.0 (3)
C28-C26-C29	111.4 (3)
C21-C26-C27	111.3 (4)
C28-C26-C27	109.0 (4)
C29-C26-C27	106.1 (3)
C26-C27-H27A	108 (3)
C26-C27-H27B	114 (3)
H27A-C27-H27B	115 (4)
C26-C27-H27C	110 (2)
H27A-C27-H27C	113 (3)
H27B-C27-H27C	97 (3)
C26-C28-H28A	113 (2)
C26-C28-H28B	111 (3)
H28A-C28-H28B	111 (3)
C26-C28-H28C	110 (2)
H28A-C28-H28C	109 (3)
H28B-C28-H28C	104 (3)
C34-C29-C30	116.1 (4)
C34-C29-C26	121.9 (4)
C30-C29-C26	121.9 (4)
C31-C30-C29	122.5 (5)
C31-C30-H30	122 (2)
C29-C30-H30	115 (2)
C32-C31-C30	119.2 (4)
C32-C31-H31	119 (3)
C30-C31-H31	121 (3)
C31-C32-C33	120.4 (4)
C31-C32-Br2	120.0 (3)
C33-C32-Br2	119.6 (4)
C32-C33-C34	119.3 (5)
C32-C33-H33	122 (3)
C34-C33-H33	119 (3)
C29-C34-C33	122.4 (5)
C29-C34-H34	120 (3)
C33-C34-H34	118 (3)
C11'-Zr'-C12'	93.54 (4)
C11'-Zr'-C4'	136.34 (11)

C12'-Zr'-C4'	98.98(10)
C11'-Zr'-C23'	99.56(11)
C12'-Zr'-C23'	137.07(11)
C4'-Zr'-C23'	99.08(14)
C11'-Zr'-C5'	114.85(10)
C12'-Zr'-C5'	130.71(10)
C4'-Zr'-C5'	33.08(13)
C23'-Zr'-C5'	79.30(14)
C11'-Zr'-C22'	130.91(9)
C12'-Zr'-C22'	113.95(10)
C4'-Zr'-C22'	80.71(13)
C23'-Zr'-C22'	33.30(13)
C5'-Zr'-C22'	77.73(13)
C11'-Zr'-C3'	112.24(10)
C12'-Zr'-C3'	78.37(10)
C4'-Zr'-C3'	33.10(12)
C23'-Zr'-C3'	131.14(14)
C5'-Zr'-C3'	54.26(13)
C22'-Zr'-C3'	112.66(13)
C11'-Zr'-C24'	78.14(11)
C12'-Zr'-C24'	114.52(12)
C4'-Zr'-C24'	131.04(14)
C23'-Zr'-C24'	32.53(14)
C5'-Zr'-C24'	110.42(14)
C22'-Zr'-C24'	53.92(14)
C3'-Zr'-C24'	163.68(14)
C11'-Zr'-C25'	92.23(9)
C12'-Zr'-C25'	85.12(10)
C4'-Zr'-C25'	130.26(13)
C23'-Zr'-C25'	53.9(2)
C5'-Zr'-C25'	129.71(13)
C22'-Zr'-C25'	53.49(13)
C3'-Zr'-C25'	151.03(14)
C24'-Zr'-C25'	32.15(14)
C11'-Zr'-C2'	83.42(10)
C12'-Zr'-C2'	94.32(9)
C4'-Zr'-C2'	54.16(13)
C23'-Zr'-C2'	127.57(14)
C5'-Zr'-C2'	53.52(12)
C22'-Zr'-C2'	130.40(13)
C3'-Zr'-C2'	32.38(13)
C24'-Zr'-C2'	146.4(2)
C25'-Zr'-C2'	175.58(13)
C11'-Zr'-C21'	124.17(8)
C12'-Zr'-C21'	84.90(8)
C4'-Zr'-C21'	98.62(12)
C23'-Zr'-C21'	54.03(13)
C5'-Zr'-C21'	107.31(12)
C22'-Zr'-C21'	32.17(11)
C3'-Zr'-C21'	121.84(12)
C24'-Zr'-C21'	53.21(13)
C25'-Zr'-C21'	31.96(11)
C2'-Zr'-C21'	152.40(12)
C11'-Zr'-C1'	84.98(8)
C12'-Zr'-C1'	126.48(8)
C4'-Zr'-C1'	54.17(13)
C23'-Zr'-C1'	95.45(14)
C5'-Zr'-C1'	32.12(11)

C22'-Zr'-C1'	106.39(12)
C3'-Zr'-C1'	53.83(13)
C24'-Zr'-C1'	117.37(14)
C25'-Zr'-C1'	148.36(13)
C2'-Zr'-C1'	32.25(11)
C21'-Zr'-C1'	138.05(11)
C5'-C1'-C2'	106.2(3)
C5'-C1'-C6'	125.9(3)
C2'-C1'-C6'	127.5(3)
C5'-C1'-Zr'	69.9(2)
C2'-C1'-Zr'	72.2(2)
C6'-C1'-Zr'	128.8(2)
C3'-C2'-C1'	108.7(3)
C3'-C2'-Zr'	71.8(2)
C1'-C2'-Zr'	75.6(2)
C3'-C2'-H2'	129(2)
C1'-C2'-H2'	122(2)
Zr'-C2'-H2'	120(2)
C4'-C3'-C2'	107.7(4)
C4'-C3'-Zr'	71.2(2)
C2'-C3'-Zr'	75.8(2)
C4'-C3'-H3'	123(2)
C2'-C3'-H3'	129(2)
Zr'-C3'-H3'	114(2)
C5'-C4'-C3'	108.0(4)
C5'-C4'-Zr'	75.4(2)
C3'-C4'-Zr'	75.7(2)
C5'-C4'-H4'	128(2)
C3'-C4'-H4'	125(2)
Zr'-C4'-H4'	114(2)
C4'-C5'-C1'	109.4(4)
C4'-C5'-Zr'	71.5(2)
C1'-C5'-Zr'	78.0(2)
C4'-C5'-H5'	125(3)
C1'-C5'-H5'	126(3)
Zr'-C5'-H5'	117(2)
C1'-C6'-C8'	110.5(3)
C1'-C6'-C9'	107.0(3)
C8'-C6'-C9'	111.3(3)
C1'-C6'-C7'	111.7(3)
C8'-C6'-C7'	108.1(4)
C9'-C6'-C7'	108.2(3)
C6'-C7'-H7D	112(2)
C6'-C7'-H7E	108(2)
H7D-C7'-H7E	113(3)
C6'-C7'-H7F	109(3)
H7D-C7'-H7F	105(4)
H7E-C7'-H7F	111(4)
C6'-C8'-H8D	107(2)
C6'-C8'-H8E	112(3)
H8D-C8'-H8E	111(4)
C6'-C8'-H8F	114(2)
H8D-C8'-H8F	109(3)
H8E-C8'-H8F	104(3)
C14'-C9'-C10'	116.9(4)
C14'-C9'-C6'	123.3(3)
C10'-C9'-C6'	119.7(3)
C11'-C10'-C9'	121.9(4)

C11'-C10'-H10'	119 (2)
C9'-C10'-H10'	119 (2)
C12'-C11'-C10'	119.0 (4)
C12'-C11'-H11'	119 (3)
C10'-C11'-H11'	122 (3)
C11'-C12'-C13'	120.8 (4)
C11'-C12'-Br1'	120.2 (3)
C13'-C12'-Br1'	119.0 (3)
C14'-C13'-C12'	119.1 (4)
C14'-C13'-H13'	122 (3)
C12'-C13'-H13'	119 (3)
C13'-C14'-C9'	122.1 (4)
C13'-C14'-H14'	123 (2)
C9'-C14'-H14'	114 (2)
C22'-C21'-C25'	106.7 (4)
C22'-C21'-C26'	124.8 (3)
C25'-C21'-C26'	127.4 (3)
C22'-C21'-Zr'	70.3 (2)
C25'-C21'-Zr'	72.0 (2)
C26'-C21'-Zr'	132.0 (2)
C21'-C22'-C23'	108.3 (4)
C21'-C22'-Zr'	77.6 (2)
C23'-C22'-Zr'	71.7 (2)
C21'-C22'-H22'	129 (3)
C23'-C22'-H22'	122 (3)
Zr'-C22'-H22'	118 (2)
C24'-C23'-C22'	107.6 (4)
C24'-C23'-Zr'	75.6 (2)
C22'-C23'-Zr'	75.0 (2)
C24'-C23'-H23'	128 (3)
C22'-C23'-H23'	124 (3)
Zr'-C23'-H23'	116 (3)
C23'-C24'-C25'	108.7 (4)
C23'-C24'-Zr'	71.8 (2)
C25'-C24'-Zr'	75.4 (2)
C23'-C24'-H24'	128 (3)
C25'-C24'-H24'	123 (3)
Zr'-C24'-H24'	116 (2)
C24'-C25'-C21'	108.6 (4)
C24'-C25'-Zr'	72.4 (2)
C21'-C25'-Zr'	76.0 (2)
C24'-C25'-H25'	128 (2)
C21'-C25'-H25'	124 (2)
Zr'-C25'-H25'	120 (2)
C21'-C26'-C28'	110.2 (3)
C21'-C26'-C27'	111.8 (3)
C28'-C26'-C27'	109.2 (4)
C21'-C26'-C29'	107.5 (3)
C28'-C26'-C29'	111.2 (3)
C27'-C26'-C29'	107.0 (3)
C26'-C27'-H27D	107 (2)
C26'-C27'-H27E	110 (2)
H27D-C27'-H27E	108 (3)
C26'-C27'-H27F	107 (3)
H27D-C27'-H27F	113 (3)
H27E-C27'-H27F	112 (3)
C26'-C28'-H28D	112 (2)
C26'-C28'-H28E	110 (2)

H28D-C28'-H28E	112 (3)
C26'-C28'-H28F	112 (2)
H28D-C28'-H28F	105 (3)
H28E-C28'-H28F	106 (4)
C34'-C29'-C30'	117.6 (4)
C34'-C29'-C26'	122.4 (3)
C30'-C29'-C26'	119.9 (3)
C29'-C30'-C31'	121.9 (4)
C29'-C30'-H30'	118 (3)
C31'-C30'-H30'	120 (3)
C32'-C31'-C30'	118.9 (4)
C32'-C31'-H31'	120 (2)
C30'-C31'-H31'	121 (2)
C33'-C32'-C31'	120.9 (4)
C33'-C32'-Br2'	118.9 (3)
C31'-C32'-Br2'	120.2 (3)
C32'-C33'-C34'	119.6 (4)
C32'-C33'-H33'	119 (2)
C34'-C33'-H33'	121 (2)
C29'-C34'-C33'	121.2 (4)
C29'-C34'-H34'	124 (2)
C33'-C34'-H34'	114 (2)

Symmetry transformations used to generate equivalent atoms:

Table A-4c. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 4-3.
 The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Zr	23(1)	17(1)	28(1)	-1(1)	11(1)	0(1)
Br1	59(1)	52(1)	39(1)	20(1)	7(1)	-10(1)
Br2	54(1)	47(1)	37(1)	-13(1)	7(1)	1(1)
Cl1	40(1)	22(1)	47(1)	5(1)	26(1)	0(1)
Cl2	39(1)	22(1)	51(1)	-8(1)	26(1)	0(1)
C1	21(2)	22(2)	29(2)	-1(2)	9(2)	-3(2)
C2	27(2)	26(2)	26(2)	-3(2)	6(2)	-5(2)
C3	20(2)	45(3)	32(2)	8(2)	15(2)	-2(2)
C4	33(3)	27(2)	27(2)	-1(2)	9(2)	7(2)
C5	22(2)	24(2)	24(2)	-2(2)	4(2)	-1(2)
C6	33(3)	31(2)	29(2)	-1(2)	15(2)	-5(2)
C7	57(4)	45(3)	38(3)	-12(2)	28(3)	-4(3)
C8	37(3)	51(4)	45(3)	8(3)	23(3)	-1(3)
C9	35(3)	29(2)	25(2)	-4(2)	15(2)	-8(2)
C10	37(3)	43(3)	40(3)	-6(2)	22(3)	-8(2)
C11	57(4)	34(3)	28(3)	2(2)	22(3)	-13(2)
C12	41(3)	37(3)	22(2)	3(2)	2(2)	-15(2)
C13	31(3)	53(3)	42(3)	18(2)	14(3)	-3(2)
C14	31(3)	54(3)	34(3)	17(2)	15(2)	-6(2)
C21	22(2)	22(2)	23(2)	0(2)	9(2)	1(2)
C22	23(2)	21(2)	29(2)	-2(2)	6(2)	1(2)
C23	24(3)	32(3)	25(2)	-2(2)	9(2)	-9(2)
C24	21(2)	42(3)	34(2)	-5(2)	13(2)	2(2)
C25	28(3)	23(2)	36(2)	0(2)	9(2)	5(2)
C26	32(3)	26(2)	29(2)	4(2)	13(2)	5(2)
C27	43(4)	41(3)	36(3)	10(2)	17(3)	2(3)
C28	32(3)	36(3)	41(3)	-1(2)	18(3)	3(2)
C29	30(3)	30(2)	27(2)	5(2)	8(2)	10(2)
C30	31(3)	38(3)	32(2)	4(2)	17(2)	6(2)
C31	47(3)	39(3)	26(2)	2(2)	16(2)	11(2)
C32	35(3)	32(2)	23(2)	-1(2)	3(2)	11(2)
C33	31(3)	57(3)	53(3)	-14(3)	11(3)	1(3)
C34	37(3)	51(3)	42(3)	-21(2)	12(3)	8(3)
Zr'	23(1)	15(1)	20(1)	-1(1)	8(1)	-1(1)
Br1'	30(1)	35(1)	57(1)	2(1)	11(1)	9(1)
Br2'	31(1)	34(1)	33(1)	-3(1)	4(1)	-9(1)
Cl1'	37(1)	21(1)	32(1)	2(1)	14(1)	-6(1)
Cl2'	37(1)	24(1)	34(1)	-4(1)	16(1)	5(1)
C1'	15(2)	21(2)	21(2)	1(2)	3(2)	1(2)
C2'	27(2)	21(2)	21(2)	-2(2)	4(2)	-2(2)
C3'	25(2)	30(2)	18(2)	0(2)	6(2)	5(2)
C4'	21(2)	28(2)	24(2)	4(2)	5(2)	-3(2)
C5'	24(2)	18(2)	21(2)	-1(2)	2(2)	1(2)
C6'	30(3)	28(2)	24(2)	-5(2)	11(2)	-6(2)
C7'	26(3)	32(3)	35(3)	1(2)	12(2)	-8(2)
C8'	30(3)	45(3)	29(3)	-4(2)	15(2)	-5(2)
C9'	22(2)	25(2)	30(2)	-3(2)	14(2)	-3(2)
C10'	26(3)	31(2)	35(2)	-12(2)	8(2)	5(2)
C11'	26(3)	37(3)	34(3)	-8(2)	6(2)	1(2)
C12'	22(2)	28(2)	43(3)	-2(2)	18(2)	-2(2)

C13'	29 (3)	23 (2)	46 (3)	-8 (2)	19 (2)	-4 (2)
C14'	28 (3)	33 (2)	30 (2)	-6 (2)	13 (2)	-5 (2)
C21'	19 (2)	18 (2)	18 (2)	0 (2)	4 (2)	0 (2)
C22'	22 (2)	19 (2)	24 (2)	-5 (2)	6 (2)	-5 (2)
C23'	24 (3)	32 (3)	29 (2)	-13 (2)	10 (2)	-2 (2)
C24'	46 (3)	39 (3)	16 (2)	-4 (2)	15 (2)	-19 (2)
C25'	28 (3)	23 (2)	24 (2)	0 (2)	3 (2)	-6 (2)
C26'	21 (2)	23 (2)	27 (2)	-3 (2)	9 (2)	4 (2)
C27'	20 (3)	28 (3)	54 (3)	-10 (2)	7 (2)	2 (2)
C28'	31 (3)	41 (3)	31 (3)	1 (2)	18 (2)	-1 (2)
C29'	18 (2)	19 (2)	24 (2)	4 (2)	6 (2)	4 (2)
C30'	25 (3)	31 (2)	30 (2)	1 (2)	14 (2)	2 (2)
C31'	23 (3)	30 (2)	36 (2)	1 (2)	13 (2)	-5 (2)
C32'	15 (2)	26 (2)	29 (2)	2 (2)	2 (2)	-2 (2)
C33'	25 (3)	34 (2)	20 (2)	-1 (2)	6 (2)	1 (2)
C34'	21 (2)	37 (3)	25 (2)	-1 (2)	11 (2)	-4 (2)

Table A-4d. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 4-3.

	x	y	z	U(eq)
H2	8705 (19)	1533 (27)	-1199 (17)	29 (11)
H3	9082 (18)	886 (25)	-2193 (16)	20 (10)
H4	8499 (21)	-724 (28)	-2530 (19)	33 (12)
H5	7802 (18)	-1245 (27)	-1821 (16)	26 (10)
H7A	8671 (25)	1286 (31)	-77 (20)	52 (14)
H7B	7800 (26)	1647 (36)	-521 (23)	69 (17)
H7C	7921 (22)	1017 (29)	87 (20)	42 (13)
H8A	7108 (22)	-878 (31)	-1061 (20)	44 (13)
H8B	7084 (22)	-312 (32)	-468 (21)	49 (14)
H8C	6909 (23)	256 (32)	-1192 (21)	53 (14)
H10	7837 (21)	-1152 (27)	302 (18)	30 (12)
H11	8607 (24)	-2194 (33)	1051 (22)	60 (16)
H13	10053 (21)	-1620 (28)	218 (19)	32 (12)
H14	9333 (21)	-528 (29)	-492 (19)	44 (13)
H22	7128 (19)	-1185 (27)	-3231 (17)	27 (11)
H23	6479 (18)	-666 (24)	-2443 (16)	15 (10)
H24	5961 (19)	996 (26)	-2760 (17)	25 (11)
H25	6237 (20)	1558 (27)	-3790 (17)	28 (11)
H27A	6437 (23)	1286 (29)	-4860 (19)	34 (13)
H27B	7193 (24)	1656 (32)	-4493 (21)	46 (14)
H27C	7082 (23)	1088 (32)	-5151 (23)	61 (14)
H28A	7892 (17)	-824 (26)	-3915 (16)	17 (9)
H28B	7942 (21)	-120 (28)	-4498 (19)	36 (13)
H28C	8088 (20)	338 (28)	-3799 (18)	30 (11)
H30	7187 (19)	-1058 (25)	-5265 (17)	14 (10)
H31	6481 (21)	-2208 (28)	-6038 (19)	35 (12)
H33	5009 (23)	-1536 (32)	-5322 (22)	43 (15)
H34	5701 (19)	-488 (26)	-4597 (17)	16 (10)
H2'	8666 (17)	-3370 (24)	3580 (15)	12 (9)
H3'	7613 (19)	-4041 (26)	3906 (17)	28 (11)
H4'	7375 (19)	-5730 (25)	3406 (16)	18 (10)
H5'	8201 (19)	-6104 (26)	2813 (17)	23 (11)
H7D	9299 (23)	-3150 (30)	2621 (20)	52 (13)
H7E	9758 (21)	-3472 (29)	3455 (21)	44 (13)
H7F	10019 (23)	-3702 (31)	2854 (21)	44 (14)
H8D	8754 (23)	-4561 (31)	1859 (20)	49 (14)
H8E	9476 (21)	-5063 (27)	2018 (19)	26 (12)
H8F	8917 (20)	-5740 (28)	2046 (17)	29 (11)
H10'	9982 (19)	-4602 (26)	4256 (17)	27 (10)
H11'	10801 (22)	-5686 (29)	5004 (20)	44 (13)
H13'	10745 (21)	-7477 (30)	3455 (19)	45 (13)
H14'	9864 (19)	-6438 (25)	2701 (18)	25 (11)
H22'	6848 (22)	-6402 (31)	2094 (20)	50 (13)
H23'	7575 (19)	-5763 (25)	1481 (17)	16 (11)
H24'	7120 (18)	-4231 (25)	891 (17)	16 (10)
H25'	6035 (19)	-3719 (26)	1083 (17)	28 (11)
H27D	4951 (20)	-4100 (27)	1171 (19)	33 (11)
H27E	4648 (20)	-4441 (25)	1779 (17)	25 (11)
H27F	5354 (22)	-3819 (31)	1991 (20)	45 (13)
H28D	5928 (19)	-6196 (27)	2621 (17)	18 (11)
H28E	5961 (24)	-5061 (33)	2893 (22)	63 (15)

H28F	5313 (21)	-5741 (26)	2634 (18)	23 (11)
H30'	4380 (22)	-6249 (30)	1708 (20)	46 (14)
H31'	3664 (19)	-7336 (25)	897 (17)	19 (10)
H33'	4974 (19)	-7227 (26)	-143 (17)	28 (11)
H34'	5679 (20)	-6135 (26)	646 (18)	31 (11)

Table A-5a. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **6-1b**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Zr	2678 (1)	7952 (1)	3330 (1)	17 (1)
Br	2991 (1)	15449 (1)	-463 (1)	39 (1)
Si	-242 (1)	8894 (1)	3260 (1)	19 (1)
N1	1338 (2)	9599 (2)	2735 (2)	21 (1)
N2	3983 (2)	8111 (2)	4396 (2)	24 (1)
N3	3865 (2)	8232 (2)	1559 (2)	24 (1)
C1	358 (2)	7143 (2)	4080 (2)	18 (1)
C2	858 (2)	6589 (2)	5295 (2)	20 (1)
C2'	358 (2)	6912 (2)	6440 (2)	27 (1)
C3	1856 (2)	5665 (2)	5262 (2)	23 (1)
C3'	2619 (3)	4778 (2)	6323 (3)	33 (1)
C4	1973 (2)	5592 (2)	4041 (2)	24 (1)
C4'	2849 (3)	4628 (3)	3681 (3)	33 (1)
C5	1035 (2)	6466 (2)	3333 (2)	21 (1)
C5'	826 (3)	6662 (3)	2014 (2)	30 (1)
C6	-1394 (2)	9430 (3)	4409 (3)	28 (1)
C7	-1156 (3)	9222 (3)	1904 (3)	30 (1)
C8	1690 (2)	10956 (2)	2013 (2)	21 (1)
C9	928 (3)	11899 (2)	1136 (2)	28 (1)
C10	1305 (3)	13224 (2)	419 (2)	30 (1)
C11	2450 (2)	13631 (2)	563 (2)	27 (1)
C12	3226 (2)	12742 (2)	1422 (2)	28 (1)
C13	2845 (2)	11415 (2)	2144 (2)	25 (1)
C14	5287 (3)	8731 (3)	3695 (3)	34 (1)
C15	3852 (3)	7727 (3)	5801 (2)	31 (1)
C16	3611 (3)	8943 (3)	216 (2)	36 (1)
C17	5016 (3)	7372 (3)	1614 (3)	39 (1)

Table A-5b. Bond lengths [Å] and angles [deg] for 6-1b.

Zr-N3	2.050 (2)
Zr-N2	2.082 (2)
Zr-N1	2.150 (2)
Zr-C1	2.466 (2)
Zr-C5	2.503 (2)
Zr-C4	2.551 (2)
Zr-C2	2.558 (2)
Zr-C3	2.593 (2)
Br-C11	1.916 (2)
Si-N1	1.740 (2)
Si-C6	1.869 (2)
Si-C7	1.878 (2)
Si-C1	1.880 (2)
N1-C8	1.414 (3)
N2-C15	1.458 (3)
N2-C14	1.462 (3)
N3-C16	1.456 (3)
N3-C17	1.458 (3)
C1-C2	1.442 (3)
C1-C5	1.446 (3)
C2-C3	1.408 (3)
C2-C2'	1.514 (3)
C2'-H2'A	0.95 (3)
C2'-H2'B	0.97 (3)
C2'-H2'C	1.00 (3)
C3-C4	1.438 (3)
C3-C3'	1.506 (3)
C3'-H3'A	0.93 (3)
C3'-H3'B	1.01 (4)
C3'-H3'C	0.98 (4)
C4-C5	1.414 (3)
C4-C4'	1.507 (3)
C4'-H4'A	1.00 (3)
C4'-H4'B	0.98 (3)
C4'-H4'C	0.91 (4)
C5-C5'	1.502 (3)
C5'-H5'A	0.99 (3)
C5'-H5'B	0.88 (4)
C5'-H5'C	0.90 (5)
C6-H6A	0.92 (3)
C6-H6B	0.89 (3)
C6-H6C	0.95 (4)
C7-H7A	0.88 (3)
C7-H7B	0.94 (3)
C7-H7C	1.02 (3)
C8-C9	1.406 (3)
C8-C13	1.406 (3)
C9-C10	1.391 (3)
C9-H9	0.91 (3)
C10-C11	1.375 (4)
C10-H10	0.96 (3)
C11-C12	1.383 (3)
C12-C13	1.393 (3)
C12-H12	0.86 (3)

C13-H13	0.97 (2)
C14-H14A	1.05 (3)
C14-H14B	1.04 (3)
C14-H14C	0.96 (3)
C15-H15A	1.01 (3)
C15-H15B	0.99 (3)
C15-H15C	0.98 (3)
C16-H16A	0.99 (3)
C16-H16B	0.99 (3)
C16-H16C	1.01 (3)
C17-H17A	1.04 (3)
C17-H17B	0.92 (3)
C17-H17C	1.00 (3)
N3-Zr-N2	104.18 (7)
N3-Zr-N1	102.48 (7)
N2-Zr-N1	112.26 (7)
N3-Zr-C1	124.71 (7)
N2-Zr-C1	129.90 (7)
N1-Zr-C1	70.15 (7)
N3-Zr-C5	95.48 (7)
N2-Zr-C5	144.41 (7)
N1-Zr-C5	91.50 (7)
C1-Zr-C5	33.82 (6)
N3-Zr-C4	95.97 (7)
N2-Zr-C4	114.78 (7)
N1-Zr-C4	122.69 (7)
C1-Zr-C4	55.03 (7)
C5-Zr-C4	32.48 (7)
N3-Zr-C2	148.20 (7)
N2-Zr-C2	98.00 (7)
N1-Zr-C2	89.56 (7)
C1-Zr-C2	33.29 (6)
C5-Zr-C2	54.40 (7)
C4-Zr-C2	53.58 (7)
N3-Zr-C3	124.60 (7)
N2-Zr-C3	90.69 (7)
N1-Zr-C3	120.67 (7)
C1-Zr-C3	54.46 (7)
C5-Zr-C3	53.86 (7)
C4-Zr-C3	32.45 (7)
C2-Zr-C3	31.71 (6)
N1-Si-C6	113.46 (10)
N1-Si-C7	115.43 (10)
C6-Si-C7	105.49 (12)
N1-Si-C1	94.77 (9)
C6-Si-C1	114.48 (11)
C7-Si-C1	113.43 (11)
C8-N1-Si	128.11 (14)
C8-N1-Zr	126.74 (14)
Si-N1-Zr	105.08 (8)
C15-N2-C14	108.8 (2)
C15-N2-Zr	131.8 (2)
C14-N2-Zr	119.4 (2)
C16-N3-C17	110.9 (2)
C16-N3-Zr	130.4 (2)
C17-N3-Zr	117.1 (2)
C2-C1-C5	106.5 (2)

C2-C1-Si	123.4 (2)
C5-C1-Si	122.5 (2)
C2-C1-Zr	76.86 (11)
C5-C1-Zr	74.47 (11)
Si-C1-Zr	89.89 (8)
C3-C2-C1	108.8 (2)
C3-C2-C2'	125.5 (2)
C1-C2-C2'	125.6 (2)
C3-C2-Zr	75.51 (12)
C1-C2-Zr	69.85 (11)
C2'-C2-Zr	122.42 (14)
C2-C2'-H2'A	112 (2)
C2-C2'-H2'B	114 (2)
H2'A-C2'-H2'B	107 (2)
C2-C2'-H2'C	111 (2)
H2'A-C2'-H2'C	106 (2)
H2'B-C2'-H2'C	106 (2)
C2-C3-C4	108.0 (2)
C2-C3-C3'	128.9 (2)
C4-C3-C3'	122.9 (2)
C2-C3-Zr	72.78 (12)
C4-C3-Zr	72.17 (12)
C3'-C3-Zr	124.9 (2)
C3-C3'-H3'A	115 (2)
C3-C3'-H3'B	110 (2)
H3'A-C3'-H3'B	105 (3)
C3-C3'-H3'C	110 (2)
H3'A-C3'-H3'C	105 (3)
H3'B-C3'-H3'C	112 (3)
C5-C4-C3	108.1 (2)
C5-C4-C4'	127.1 (2)
C3-C4-C4'	124.5 (2)
C5-C4-Zr	71.88 (11)
C3-C4-Zr	75.38 (12)
C4'-C4-Zr	123.7 (2)
C4-C4'-H4'A	113 (2)
C4-C4'-H4'B	111 (2)
H4'A-C4'-H4'B	109 (2)
C4-C4'-H4'C	109 (2)
H4'A-C4'-H4'C	108 (3)
H4'B-C4'-H4'C	106 (3)
C4-C5-C1	108.4 (2)
C4-C5-C5'	124.7 (2)
C1-C5-C5'	126.9 (2)
C4-C5-Zr	75.64 (12)
C1-C5-Zr	71.71 (11)
C5'-C5-Zr	117.6 (2)
C5-C5'-H5'A	113 (2)
C5-C5'-H5'B	110 (2)
H5'A-C5'-H5'B	106 (3)
C5-C5'-H5'C	115 (3)
H5'A-C5'-H5'C	105 (3)
H5'B-C5'-H5'C	109 (4)
Si-C6-H6A	114 (2)
Si-C6-H6B	106 (2)
H6A-C6-H6B	111 (3)
Si-C6-H6C	113 (2)
H6A-C6-H6C	109 (3)

H6B-C6-H6C	104 (3)
Si-C7-H7A	110 (2)
Si-C7-H7B	113 (2)
H7A-C7-H7B	110 (3)
Si-C7-H7C	112 (2)
H7A-C7-H7C	104 (3)
H7B-C7-H7C	108 (3)
C9-C8-C13	117.1 (2)
C9-C8-N1	122.5 (2)
C13-C8-N1	120.4 (2)
C10-C9-C8	121.5 (2)
C10-C9-H9	118 (2)
C8-C9-H9	120 (2)
C11-C10-C9	119.7 (2)
C11-C10-H10	119 (2)
C9-C10-H10	121 (2)
C10-C11-C12	120.9 (2)
C10-C11-Br	119.5 (2)
C12-C11-Br	119.6 (2)
C11-C12-C13	119.4 (2)
C11-C12-H12	119 (2)
C13-C12-H12	121 (2)
C12-C13-C8	121.4 (2)
C12-C13-H13	120.1 (14)
C8-C13-H13	118.4 (14)
N2-C14-H14A	113 (2)
N2-C14-H14B	111 (2)
H14A-C14-H14B	105 (2)
N2-C14-H14C	113 (2)
H14A-C14-H14C	105 (2)
H14B-C14-H14C	109 (2)
N2-C15-H15A	112 (2)
N2-C15-H15B	112 (2)
H15A-C15-H15B	107 (2)
N2-C15-H15C	111 (2)
H15A-C15-H15C	108 (2)
H15B-C15-H15C	108 (3)
N3-C16-H16A	111 (2)
N3-C16-H16B	109 (2)
H16A-C16-H16B	108 (2)
N3-C16-H16C	115 (2)
H16A-C16-H16C	104 (2)
H16B-C16-H16C	109 (2)
N3-C17-H17A	109 (2)
N3-C17-H17B	112 (2)
H17A-C17-H17B	101 (3)
N3-C17-H17C	112 (2)
H17A-C17-H17C	117 (2)
H17B-C17-H17C	106 (3)

Symmetry transformations used to generate equivalent atoms:

Table A-5c. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 6-1b.
 The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Zr	15(1)	16(1)	16(1)	-6(1)	-3(1)	-1(1)
Br	59(1)	20(1)	30(1)	-7(1)	2(1)	-11(1)
Si	16(1)	19(1)	21(1)	-8(1)	-4(1)	0(1)
N1	20(1)	18(1)	22(1)	-7(1)	-4(1)	-2(1)
N2	22(1)	25(1)	23(1)	-9(1)	-7(1)	-1(1)
N3	21(1)	27(1)	19(1)	-6(1)	0(1)	0(1)
C1	15(1)	19(1)	20(1)	-9(1)	-1(1)	-4(1)
C2	18(1)	19(1)	19(1)	-6(1)	-2(1)	-4(1)
C2'	27(1)	33(1)	20(1)	-14(1)	-2(1)	-1(1)
C3	23(1)	19(1)	22(1)	-5(1)	-3(1)	-4(1)
C3'	31(1)	24(1)	32(1)	-3(1)	-8(1)	3(1)
C4	22(1)	18(1)	29(1)	-11(1)	-1(1)	-3(1)
C4'	31(1)	27(1)	44(2)	-20(1)	-5(1)	5(1)
C5	21(1)	20(1)	23(1)	-10(1)	-1(1)	-5(1)
C5'	30(1)	39(1)	28(1)	-20(1)	-6(1)	-2(1)
C6	24(1)	29(1)	35(1)	-19(1)	-3(1)	1(1)
C7	27(1)	29(1)	32(1)	-10(1)	-13(1)	0(1)
C8	22(1)	20(1)	18(1)	-9(1)	0(1)	1(1)
C9	31(1)	24(1)	28(1)	-10(1)	-10(1)	-1(1)
C10	39(1)	24(1)	24(1)	-8(1)	-8(1)	2(1)
C11	39(1)	18(1)	19(1)	-8(1)	3(1)	-4(1)
C12	25(1)	27(1)	32(1)	-14(1)	0(1)	-6(1)
C13	23(1)	22(1)	26(1)	-9(1)	-4(1)	-1(1)
C14	28(1)	37(1)	34(1)	-9(1)	-11(1)	-9(1)
C15	30(1)	39(1)	31(1)	-20(1)	-11(1)	4(1)
C16	39(2)	42(2)	21(1)	-8(1)	-6(1)	-5(1)
C17	31(1)	39(2)	35(2)	-12(1)	1(1)	8(1)

Table A-5d. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **6-1b**.

	x	y	z	U(eq)
H2'A	-577 (29)	6784 (25)	6746 (25)	31 (7)
H2'B	551 (29)	7812 (29)	6239 (28)	40 (8)
H2'C	770 (30)	6318 (28)	7218 (29)	44 (8)
H3'A	2496 (29)	4951 (28)	7049 (29)	41 (8)
H3'B	3603 (37)	4891 (32)	5951 (33)	61 (10)
H3'C	2335 (37)	3854 (36)	6692 (34)	70 (11)
H4'A	3026 (30)	4886 (27)	2711 (30)	42 (8)
H4'B	2463 (28)	3738 (28)	4170 (27)	40 (8)
H4'C	3643 (39)	4572 (34)	3929 (34)	66 (11)
H5'A	1018 (33)	7580 (34)	1311 (33)	57 (9)
H5'B	-12 (41)	6516 (36)	2061 (35)	73 (12)
H5'C	1345 (48)	6160 (43)	1694 (43)	100 (15)
H6A	-1005 (29)	9440 (26)	5052 (29)	37 (8)
H6B	-1669 (33)	10232 (33)	3897 (31)	52 (9)
H6C	-2188 (38)	8924 (33)	4819 (33)	63 (10)
H7A	-1577 (31)	9980 (30)	1682 (28)	47 (9)
H7B	-1757 (32)	8545 (31)	2134 (30)	50 (9)
H7C	-513 (32)	9343 (29)	1051 (31)	48 (8)
H9	143 (27)	11658 (24)	1063 (24)	26 (6)
H10	738 (30)	13878 (28)	-108 (28)	42 (8)
H12	3919 (27)	13023 (24)	1524 (24)	26 (7)
H13	3369 (25)	10789 (23)	2761 (24)	25 (6)
H14A	6074 (29)	8091 (26)	4032 (27)	38 (7)
H14B	5417 (29)	9545 (29)	3844 (28)	45 (8)
H14C	5446 (29)	9008 (27)	2760 (30)	41 (8)
H15A	4540 (30)	7055 (28)	6203 (27)	40 (8)
H15B	2972 (35)	7317 (32)	6313 (31)	52 (9)
H15C	3950 (33)	8492 (32)	5939 (31)	56 (9)
H16A	4396 (32)	9475 (29)	-410 (29)	45 (8)
H16B	2857 (34)	9561 (30)	192 (30)	51 (9)
H16C	3424 (29)	8365 (29)	-180 (28)	44 (8)
H17A	5201 (31)	6917 (29)	2578 (31)	51 (9)
H17B	5788 (33)	7851 (29)	1144 (30)	45 (8)
H17C	4941 (32)	6782 (30)	1209 (31)	50 (9)

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BIOGRAPHICAL SKETCH

The author was born in Scranton, Pennsylvania and grew up outside Philadelphia in the small town of Trooper, Pennsylvania. After considering becoming a lawyer, psychologist, commercial helicopter pilot, or bounty hunter, an interest in chemistry was sparked by an outstanding teacher, Angela B. Bacher, while at Methacton High School.

Following graduation in 1988 the author moved to the College of Wooster to pursue studies in chemistry and German. Four years later, he graduated from Wooster with a B.A. in chemistry, the ability to address and solve problems, and many great memories of four wonderful years. An interest in synthetic organometallic chemistry was initiated by his research advisor, Professor Paul Gaus, and he chose to continue his studies of chemistry in graduate school at the University of Florida.

After five years of intense research under Professors David Richardson and James Boncella, the author completed the requirements for a Doctor of Philosophy degree in inorganic chemistry in the spring of 1997, shortly after getting married to his lovely wife, Heather. The author has accepted an offer of employment with Bridgestone/Firestone Research in Akron, Ohio, and looks forward to entering the "real world."

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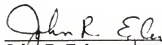
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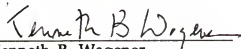
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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry of the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 1997

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